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COATING/HARDMASK MATERIALS

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1.   U.S. Patent Application Publication No. 2005/0074699 A1 to Sun et al., published on

April 7, 2005, from U.S. Patent Application No. 10/864,787, filed June 8, 2004.

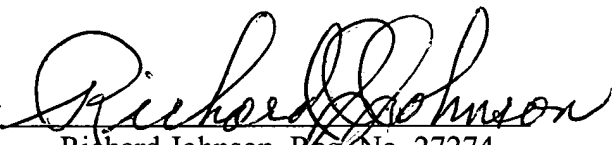A check for the sum of $180.00 is enclosed to cover the submission fee under 37 CFR

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Respectfully submitted,

By _____

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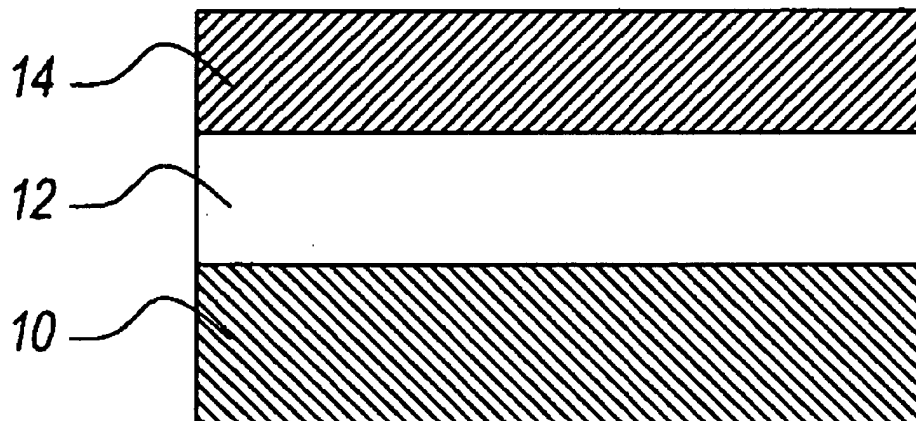5612 18th Street North
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(54) **WATER AND AQUEOUS BASE SOLUBLE ANTIREFLECTIVE COATING/HARDMASK MATERIALS**

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(57) **ABSTRACT**

A multilayer lithographic structure which includes a substrate, having on a major surface thereof a first layer including a water and/or aqueous base soluble material which includes Ge, O, and H, and optionally X, wherein X is at least one of Si, N, and F; and disposed on the first layer a second layer which includes an energy photoactive material.

14 —

12 —

10 —

Fig. 1(a)
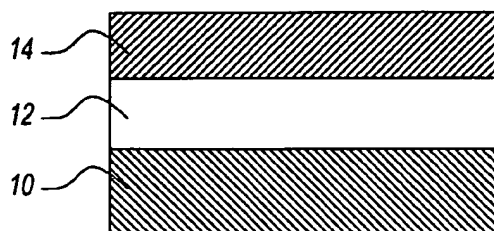
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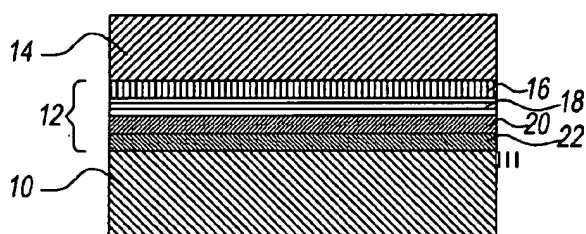
12 {

10 —

16
18
20
22
III

Fig. 1(b)

14 —

12 {

10 —

— 24

Fig. 1(c)

14 —

12 —

10 —

— 26
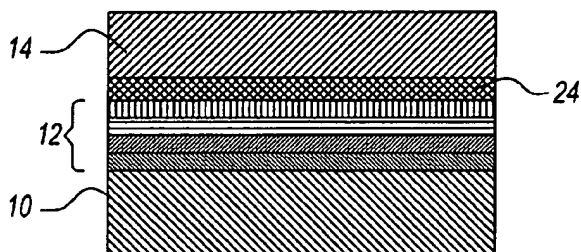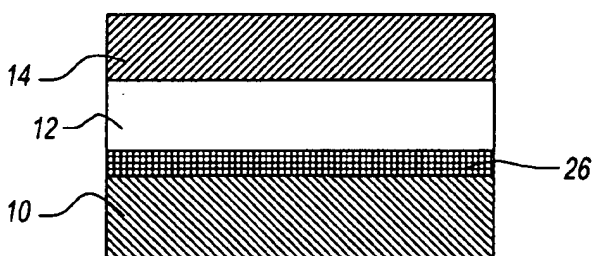
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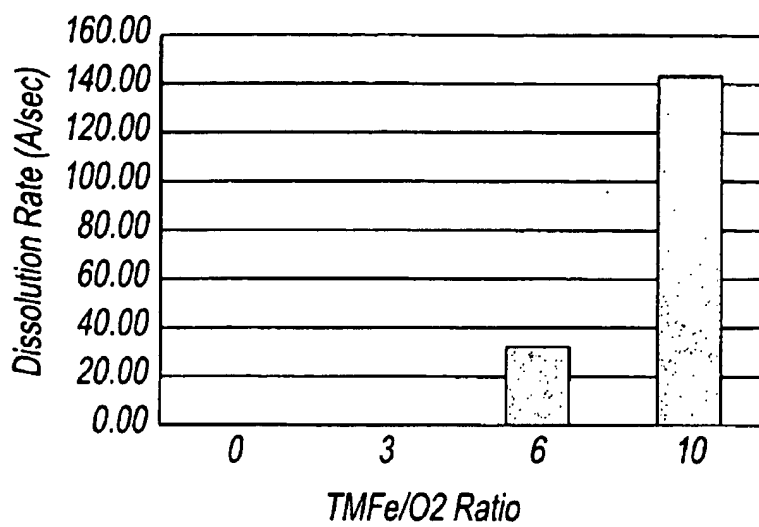
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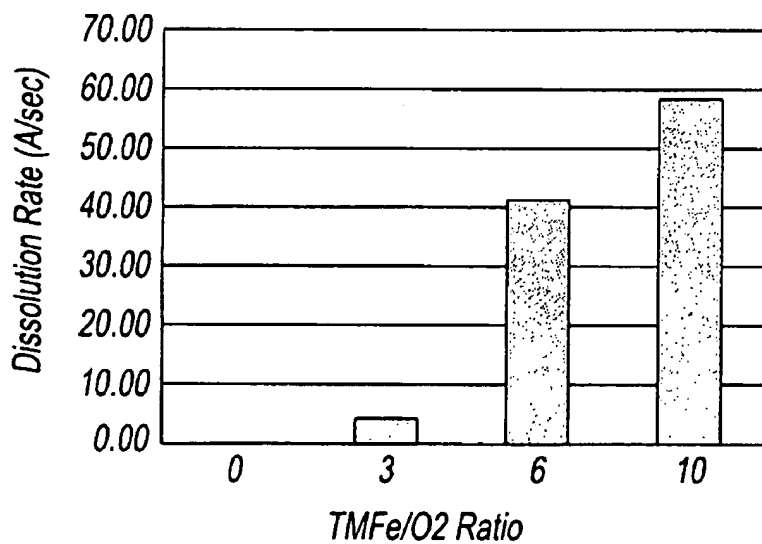
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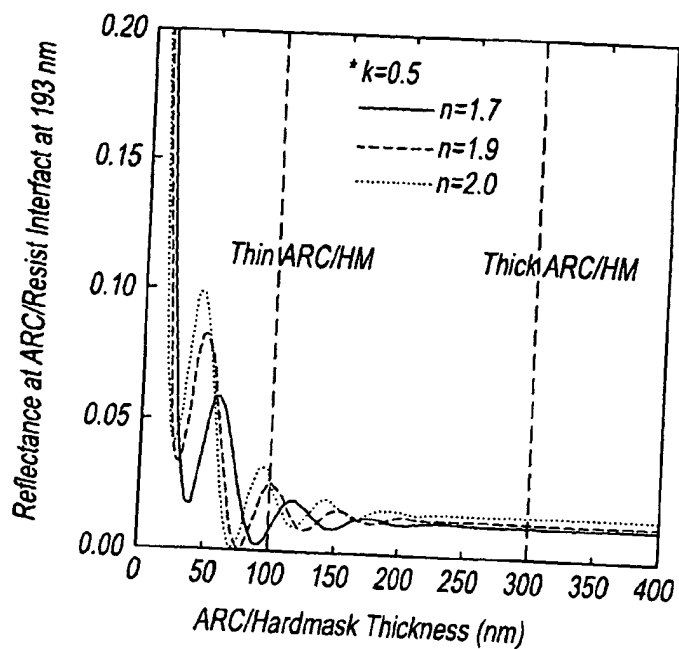
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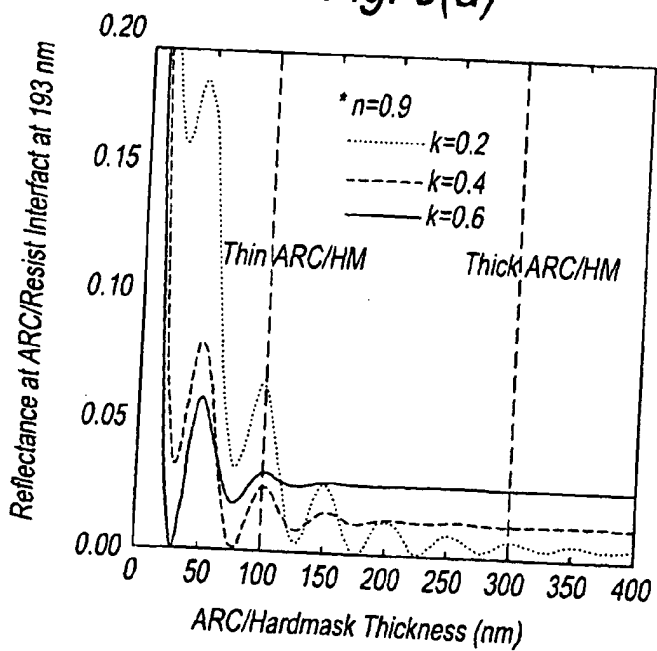
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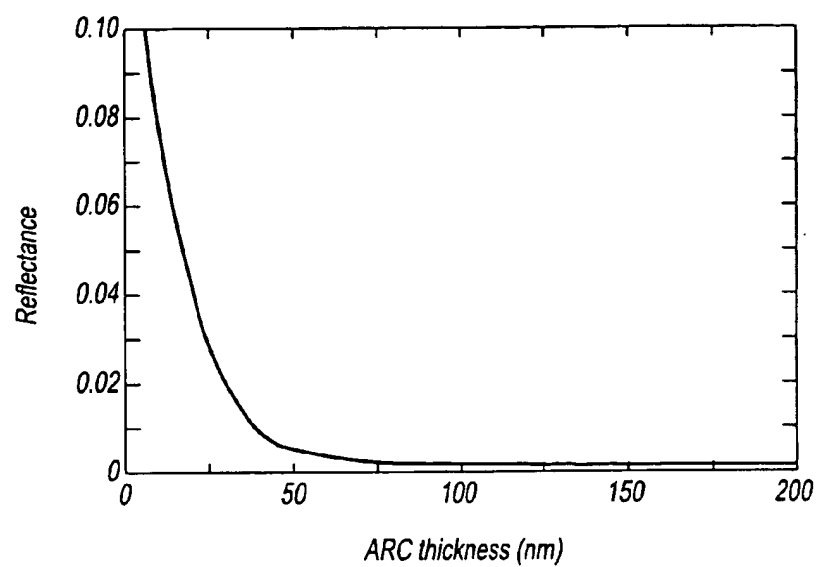
Fig. 4

Fig. 5(a)

Fig. 5(b)

Fig. 6

34 — 30 — 32 —

Fig. 7(a)

38 — 34 — 36 — 30 — 32 —

Fig. 7(b)

38 — 36 — 34 — 36 — 30 — 32 —

Fig. 7(c)

36

34

30

36

32

Fig. 7(d)

34

34

30

30

32

Fig. 7(e)

44 — 40 — 42 —

Fig. 8(a)

48 — 46 — 44 — 40 — 42 — — 44 — 40

Fig. 8(b)

50 — 48 — 46 — 44 — 40 — 42 — — 50 — 44 — 40

Fig. 8(c)

50 — 50
48 — 48
46 — 46
46
44 — 44
40 — 40
42

Fig. 8(d)

46 — 46
44 — 44
46
40 — 40
42

Fig. 8(e)

44 — 44
40 — 40
42
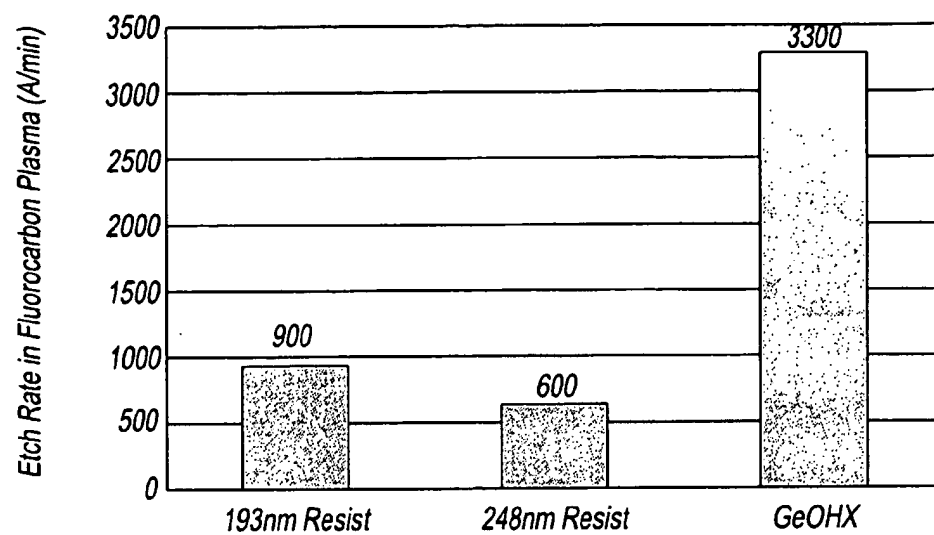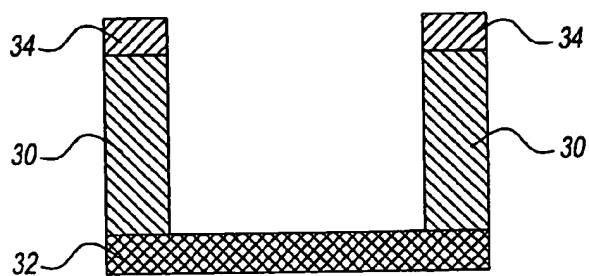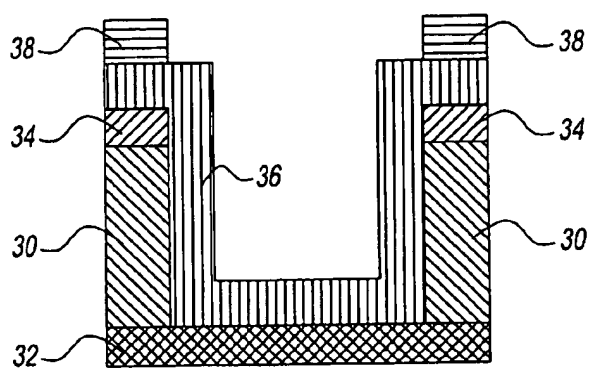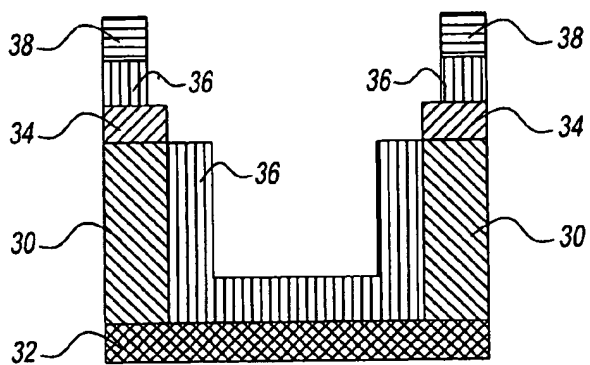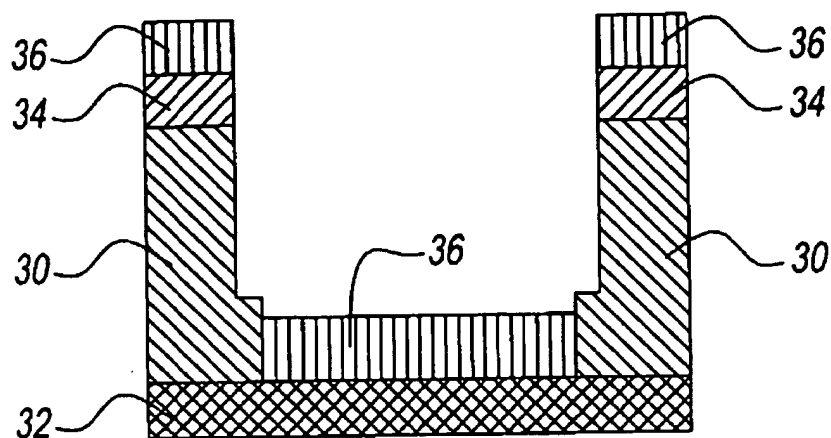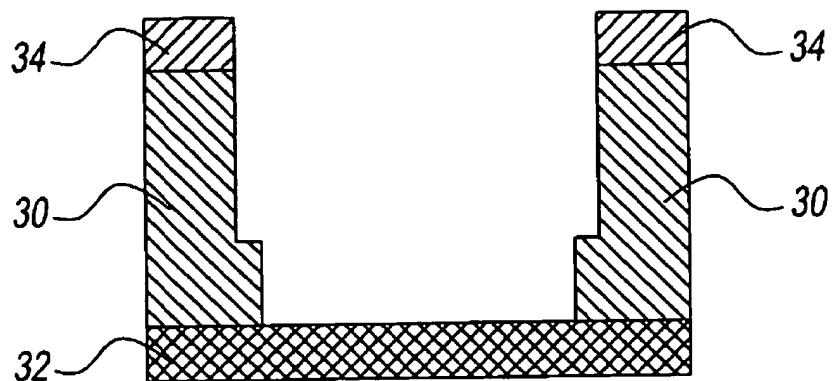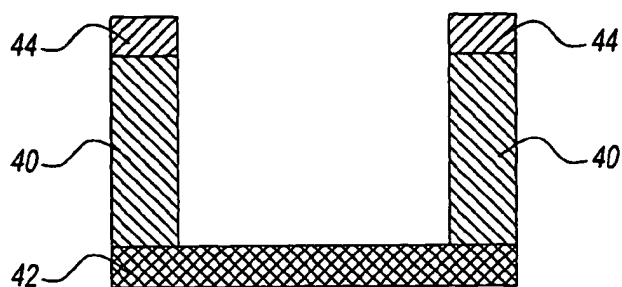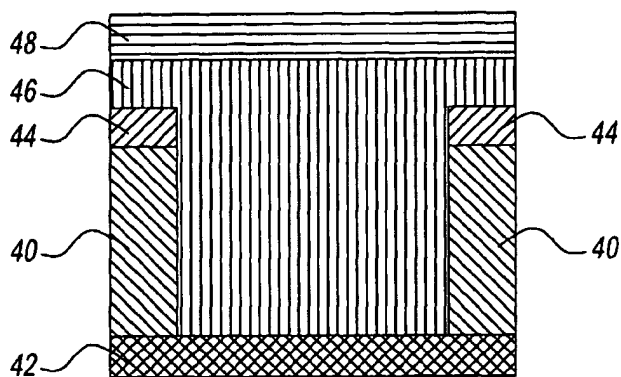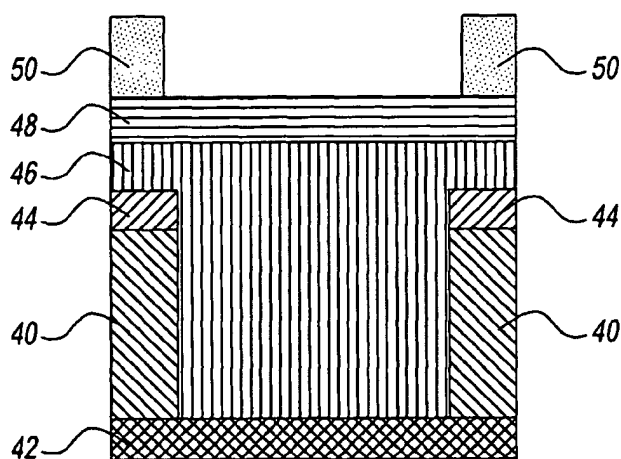
Fig. 8(f)

WATER AND AQUEOUS BASE SOLUBLE ANTIREFLECTIVE COATING/HARDMASK MATERIALS

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to films for use as antireflective coatings and hardmasks for lithographic structures. More particularly, the present invention relates to optically tunable, water and/or aqueous base soluble materials for use as antireflective coatings, hardmasks, and combined antireflective coating/hardmasks.

[0003] 2. Description of the Prior Art

[0004] The need to remain cost and performance competitive in the production of semiconductor devices has driven the industry to a continuing increase in device density with a concomitant decrease in device geometry. To facilitate the shrinking device dimensions, new lithographic materials, processes and tools are being considered. Currently, 248 nm lithography is being pursued to print sub-200 nm features. To do this, tools with higher numerical aperture (NA) are emerging. The higher NA allows for improved resolution but reduces the depth of focus of aerial images projected onto the resist. Because of the reduced depth of focus, a thinner resist will be required. As the thickness of the resist is decreased, the resist becomes less effective as a mask for subsequent dry etch image transfer to the underlying substrate, i.e. most if not all of the resist is etched away during the subsequent pattern transfer process. Without significant improvement in the etch selectivity exhibited by current single layer resists (SLR), these systems cannot provide the necessary lithographic and etch properties for high-resolution lithography.

[0005] Typical resist structures consist of a resist on top of an antireflective coating (ARC). The resist is exposed and developed and the image is then transferred through the ARC and then through the underlying layers, such as oxide, nitride or silicon layers. Typical resist thickness is on the order of 5000 A for the current state-of-the-art lithography process. During the ARC open, significant resist is lost as the etch selectivity between the resist and ARC is at best 1:1. As minimum features continue to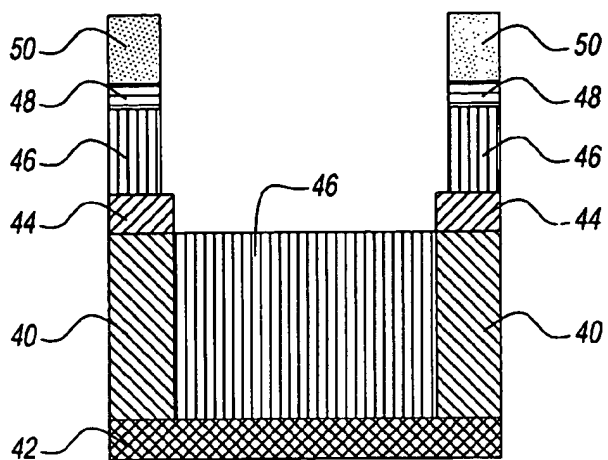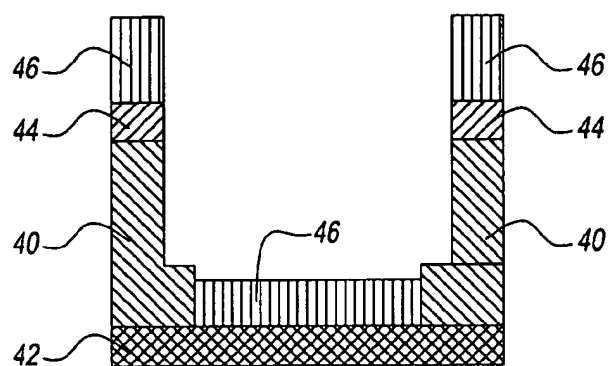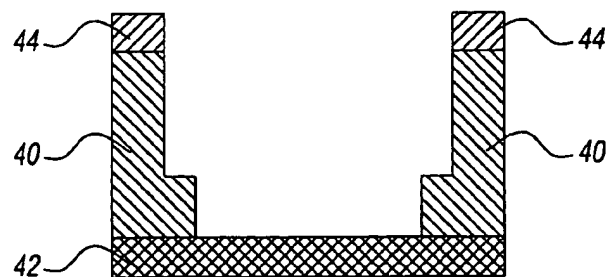 decrease, it is desirable to thin the resist to attain the high resolution as well as improved process window (exposure and focus latitude). However, thinning the resist below 5000 A poses etch problems. There may be insufficient resist to function as an etch mask for subsequent transfer etch into underlying layer. Compounding this problem is the fact that significant resist loss also occurs during the ARC open.

[0006] Another problem with single layer resist systems is critical dimension (CD) control. Substrate reflections at ultraviolet (UV) and deep ultraviolet (DUV) wavelengths are notorious for producing standing wave effects and resist notching, which severely limit CD control of single layer resists. Notching results from substrate topography and non-uniform substrate reflectivity, which causes local variations in exposure energy on the resist. Standing waves are thin film interference (TFI) or periodic variations of light intensity through the resist thickness. These light variations are introduced because planarization of the resist presents different thickness through the underlying topography. Thin

film interference plays a dominant role in CD control of single layer photoresist processes, causing large changes in the effective exposure dose due to a tiny change in optical phase. Thin film interference effects are described in "Optimization of optical properties of resist processes" (T. Brunner, SPIE Proceedings Vol. 1466, p. 297, 1991), the teaching of which is incorporated herein by reference.

[0007] Bottom anti-reflective coatings or BARCs have been used with single layer resists to reduce thin film interference. However, these thin absorbing BARCs have fundamental limitations. These materials are generally spin applied. The thickness of the BARC and the resist cannot be controlled to the accuracy required to operate at the target thickness to achieve minimum reflectance. The resist thickness can also vary due to existing topography. Thin underlying films such as silicon nitride or silicon oxide tend to exhibit some thickness non-uniformity after deposition. The thin BARC will generally not effectively planarize these thin underlying films. Thus, as a result there will be a variation in exposure energy into the resist. Current trends to reduce topography via chemical/mechanical polishing still leave significant variations in film thickness over topography.

[0008] To overcome some of the limitations of single layer resists, thin film imaging techniques have been developed including bilayer resists, trilayer resist systems and top surface imaging (TSI). In a bilayer structure, a thin resist containing Si functionality for etch resistance is coated on top of a thick polymer layer with suitable absorption at the exposing wavelength to act as a BARC and suitable etch resistance for substrate etch. Because of the thick resist/ underlayer stack, this technique offers tremendous advantage for etch transfer. However, incorporation of Si moieties into the imaging resist structure is very challenging and can result in limited resolution and low performance of such resist systems. All of these thin film imaging techniques are more complex and costly than current single layer resist processes.

[0009] The importance of hardmask technology is becoming increasingly evident as the demand for high-resolution imaging dictates the use of ever-thinner resist films. An appropriately designed etch resistant hardmask used in conjunction with a thin resist can provide the combined lithographic and etch performance needed for sub-100 nm device fabrication. Plasma-enhanced chemical vapor deposition (PECVD) prepared materials that perform both as an antireflective coating (ARC) and hardmask offer several advantages over organic bottom antireflective coatings (BARC) currently used for manufacturing of logic and memory chips. These benefits include excellent tunability of the material's optical properties, which allows superior substrate reflectivity control, high etch selectivity to resist, exceeding 2:1 due to the significant difference in chemical composition between resist and PECVD deposited material. In addition, PECVD deposited materials are highly crosslinked covalent networks which are considerably denser compared to organic materials thus can serve as an effective hardmask etch barrier during the plasma etching of dielectric stacks. In contrast, organic BARCs have poor optical tunability, which means that their index of refraction, n, and the extinction coefficient, k, cannot be finely tuned to match resist and substrate optical properties. Additionally, organic BARCs have chemical composition very similar to resist materials which results in poor etch selectivity of

about or less than 1:1 between resist and BARC to resist. Thus, about 100 nm of the resist is consumed during ARC open, with high-resolution imaging, this becomes a fundamental process limitation.

[0010] Recently, considerable interest has been focused on PECVD prepared ARC/hardmask materials as they offer tremendous leverage for extending optical lithography to sub 100 nm resolution. Such materials are described in U.S. Pat. Nos. 6,316,167 and 6,514,667. Typically, ARC/hardmask materials must be removed after the lithographic patterning is complete as their presence in the final device structure can adversely affect the device performance. The PECVD ARC/hardmask materials described in these two patents are highly cross-linked covalent networks which are significantly dense compared to organic polymer films and hence difficult to remove with conventional wet and dry strip processes without damaging the layers underneath. This significantly limits their use in semiconductor processing.

[0011] Depending on the particular integration structure, PECVD ARC/hardmask materials must be removed from the structure selective to one or more substrate materials. The substrate can be a dielectric material e.g. silicon oxide or silicon nitride, low dielectric constant materials e.g. SiCOH and ultra-low dielectric constant materials e.g. porous SiCOH and/or a semiconductor such as polysilicon and/or a metal e.g. copper, aluminum. Improved ARC/hardmask materials that can be selectively removed are needed.

[0012] It is desirable to develop a thin resist process which provides excellent lithographic performance and provides appropriate etch resistance for effective pattern transfer into the underlying substrate. In order to do this, improved ARC/hardmask materials are needed which provide better etch selectivity to resist than current organic BARCs. The ARC/hardmask material needs to (1) have appropriate optical properties to function as a suitable ARC at appropriate wavelength, (2) provide good etch selectivity to resist (greater than 1:1), and (3) does not interact with the resist inducing residue, footing, undercut thereby limiting the overall lithographic performance of the resist. It is also desirable that the ARC/hardmask material also function as a suitable hard mask material for the underlayer etch. Germanium based ARC/hardmask materials prepared by PECVD processes and spin coating processes whose properties are tailored to allow selective removal of these materials from the structure in water or aqueous base solutions are disclosed herein.

SUMMARY OF THE INVENTION

[0013] The present invention provides a multilayer lithographic structure which includes a substrate, having on a major surface thereof a first layer including a water and/or aqueous base soluble material which includes Ge, O, and H, and optionally X, wherein X is at least one of Si, N, and F; and disposed on the first layer a second layer which includes an energy photoactive material.

[0014] The present invention further provides a method of making a lithographic structure which includes depositing on a surface of a substrate a first layer which includes a water and/or aqueous base soluble material which includes Ge, O, and H, and optionally X, wherein X is at least one of Si, N,

and F; and depositing on the first layer a second layer which includes an energy photoactive material.

[0015] The present invention still further provides a film for a lithographic structure which includes a water and/or aqueous base soluble material comprising Ge, O, and H, and optionally X, wherein X is at least one of Si, N, and F.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] FIG. 1 shows four basic lithographic structures according to the present invention.

[0017] FIG. 2(a) shows the dissolution rates (A/sec) of GeOHX materials in water as a function of TMGe to O2 ratio.

[0018] FIG. 2(b) shows the dissolution rates (A/sec) of GeOHX materials in 0.26N tetramethylammoniunhydroxide (TMAH) aqueous base solution as a function of TMGe to O2 ratio.

[0019] FIG. 3(a) shows reflectance at ARC-hardmask/resist interface at 248 nm as a function of ARC thickness for different values of refractive index (n) using a fixed value of k=0.25.

[0020] FIG. 3(b) shows reflectance at ARC-hardmask/resist interface at 248 nm as a function of ARC thickness for different values of extinction coefficient (k) using a fixed value of n=1.75.

[0021] FIG. 4 shows reflectance at ARC-hardmask/resist interface at 193 nm as a function of ARC thickness for graded (layered) GeOHX material.

[0022] FIG. 5(a) shows SEM image of half-pitch line-and-space structures patterned on single layer GeOHX ARC/hardmasks material using UV82 at 248 nm giving 150 nm resolution.

[0023] FIG. 5(b) shows SEM image of high resolution half-pitch line-and-space structures patterned on multilayer SiCOH/GeOHX material using 193 nm resist giving 100 nm resolution.

[0024] FIG. 6 shows blanket etch rates of GeOHX ARC/hardmask and two photoresists in a fluorocarbon based plasma chemistry.

[0025] FIG. 7 shows a use and removal of a water and/or aqueous base soluble GeOHX ARC/hardmask material in a dual damascene integration scheme.

[0026] FIG. 8 shows a use of a water and/or aqueous base soluble GeOHX material as a planarizing spin-coated layer.

DETAILED DESCRIPTION OF THE INVENTION

[0027] The present invention provides a multilayer lithographic structure which includes a substrate, having on a major surface thereof a first layer including a water and/or aqueous base soluble material which includes Ge, O, and H, and optionally X, wherein X is at least one of Si, N, and F; and disposed on the first layer a second layer which includes an energy photoactive material.

[0028] The present invention further provides a method of making a lithographic structure which includes depositing on a surface of a substrate a first layer including a water

and/or aqueous base soluble material which includes Ge, O, and H, and optionally X, wherein X is at least one of Si, N, and F; and depositing on the first layer a second layer which includes an energy photoactive material.

[0029] The present invention still further provides a film for a lithographic structure including a water and/or aqueous base soluble material which includes Ge, O, and H, and optionally X, wherein X is at least one of Si, N, and F.

[0030] The materials or films that are useful to practice the present invention include Ge, O, and H, and optionally X, wherein X is selected from at least one of Si, N, and F. These films (GeOHX films) can be used in a lithographic structure as a first layer between a substrate and a second layer having an energy photoactive material. These materials are soluble in water and/or an aqueous base. These materials can perform a variety of functions in the lithographic structure, for example these materials can be used as a hardmask layer; an anti-reflection layer, such as a BARC; or as a combined hardmask/anti-reflection layer. The GeOHX films of the present invention may act as an anti-reflection layer in any lithographic process. Examples of lithographic processes include, but are not limited to, 248 nm, 193 nm, 157 nm, 126 nm, extreme UV, and electron beam.

[0031] A multilayer lithographic structure according to the present invention includes a substrate having on a surface thereof a first layer. The first layer includes one or more layers of a material which includes Ge, O, and H, and optionally X, wherein X is selected from at least one of Si, N, and F. The first layer is water and/or aqueous base soluble. The first layer has thereon a second layer, which includes an energy photoactive material.

[0032] When the first layer includes more than one layer of a material which includes Ge, O, and H, and optionally X, wherein X is selected from at least one of Si, N, and F, the multiple layers, or films, may be of the same composition of GeOHX or of a different composition of GeOHX. This allows for the fine tuning of the optical constants of the first layer throughout its thickness. The optical constants of the first layer can therefore substantially match those of the substrate at a first interface between the first layer and the substrate, as well as, substantially match the optical properties of the second layer at a second interface between the first layer and the second layer. The optical properties at the imaging wavelengths, such as 248, 193 or 157 nm and the lithographic features of the film produced by the present invention are vastly superior to those obtained by other hardmask materials such as oxide type materials (TEOS, BSG) and nitride type materials (H. C. Lee, J. Vac. Sci. Technol., vol. 16, No. 5, p. 2763, 1998, J. F. Rembetski, Solid State Technol. Vol. 38, No. 3, p 67, 1995). For example, a Si substrate coated with a thick planarizing-ARC-hard mask GeOHX material of this invention drastically reduces thin film interference and substrate reflectivity, which consequently improves CD control.

[0033] It is possible to vary the optical properties of the first layer over a wide range of values. For example, optimum values for the index of refraction, n, the extinction coefficient, k, and layer thickness can be obtained by modeling multilayer lithographic. Knowledge of the optical constants of the entire film structure is important to compute the minimal reflectance at the interface between the first layer and the second layer and the interface between the first

layer and the substrate. Computations are based on algorithms which use the Fresnel coefficients as found in standard textbooks such as Optics, by E. Hecht and A. Zajac, published in 1979 by Wiley, pages 312 and 313. The preferred optical constants of the films of the first layer are an index of refraction of between about 1.4 to about 2.6 and extinction coefficient of between about 0.01 to about 1. More preferably the index of refraction is between about 1.58 and 2.0 and the extinction coefficient is between about 0.01 and 0.8 at various imaging wavelengths. Table 1 includes example n and k values for various GeOHX films. More commonly, the k values were between 0.15 and 0.6 at the imaging wavelength.

[0034] The first layer can be any thickness that provides the desired optical properties. Preferably the thickness of the first layer is between about 200 Angstroms and about 5,000 Angstroms. More preferably the thickness of the first layer is between about 350 Angstroms and about 3,000 Angstroms depending on film absorption.

TABLE 1

Variation of n and k values at 193 nm and 248 nm of GeOHX ARC/hardmask PECVD films deposited at various plasma chemistries and deposition conditions showing the tunability of the antireflective properties of these materials.

Film Composition	Optical Constants					
	$n_{157\,nm}$	$k_{157\,nm}$	$n_{193\,nm}$	$k_{193\,nm}$	$n_{248\,nm}$	$k_{248\,nm}$
GeOH	—	—	1.769	0.081	1.581	0.005
GeOHX	—	—	1.841	0.467	1.929	0.127
GeOHX	—	—	1.911	0.138	1.767	0.017
GeOHX	—	—	1.842	0.532	1.957	0.164
GeOH	—	—	2.024	0.237	1.876	0.07
GeOH	—	—	1.907	0.346	1.817	0.048
GeOHX	—	—	1.966	0.387	1.948	0.256
GeOHX	—	—	1.932	0.691	2.089	0.567
GeOHX	1.567	0.829	1.795	0.775		

[0035] The second layer includes an energy photoactive material. This energy photoactive material may be a resist material. The resist material may be a chemically amplified resist material or any known energy photoactive material. Examples of suitable energy photoactive materials include, but are not limited to, IBM/JSR ARF AR series, such as AR165J and AR237J; JSR ESCAP chemistries KRF M series, such as M20G; Shipley Epic V40 and Epic S7 193 nm photoresists; Shipley UVx series, such as UV8, UV110 and other acrylates; cyclic olefin/maleic anhydride; VEMA; cyclized polymer based commercial 193 nm photoresists; and any combinations thereof. The energy active material can be sensitive to any suitable energy. Examples of suitable energies include, but are not limited to, 248 nm, 193, nm, 157 nm, 126 nm, extreme ultraviolet, electron beam, ion beam, and x-ray.

[0036] The thickness of the second layer will vary depending on the material chosen and the lithographic process, and can be any suitable thickness. The thickness of the second layer is preferably between about 1,000 Angstroms and about 3,000 Angstroms, and more preferably between about 250 Angstroms (A) and about 6,000 Angstroms (A).

[0037] The first layer can be a hardmask layer, an anti-reflection layer, or a combined hardmask/anti-reflection layer. It is also possible that a third layer may be interposed

between the first layer (GeOHX layer) and the second layer (energy photoactive layer). An example of a suitable third layer includes, but is not limited to, an anti-reflective coating, such as a BARC. When the first layer is used as a hardmask layer alone, such a BARC would be useful. The third layer can be a spin-coated polymeric BARC or a chemical vapor deposited BARC. A preferred third layer is an antireflective coating that includes R, C, O, and H, wherein R is selected from the group consisting of: Si, Ge, Ti and any combinations thereof (an RCOH layer).

[0038] A preferred RCOH layer includes a polymer having SiO moieties in its backbone. The polymer is preferably an organosiloxane, more preferably organosilsesquioxane. In general, the polymer preferably contains one or more monomers having structures selected from (I)-(III) below:

$$\begin{array}{c} R_1 \\ | \\ -SiO_x- \end{array} \quad \text{(I)}$$

$$\begin{array}{c} R_2 \\ | \\ -SiO_x- \end{array} \quad \text{(II)}$$

$$\begin{array}{c} R_3 \\ | \\ -SiO_x- \end{array} \quad \text{(III)}$$
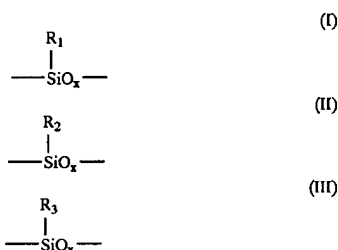
[0039] where x is from about 1 to about 1.5. R_1 comprises a chromophore moiety; R_2 comprises a transparent moiety; R_3 comprises a reactive site for reaction with a crosslinking component. For linear organosiloxane polymers, x would equal about 1. For silsesquioxane polymers, x would equal about 1.5. In some instances, multiple functional moieties may be present on the same monomer (e.g., a reactive group and a chromophore). Generally, silsesquioxane polymers are preferred on the basis of superior etch resistance. If the ordinary organosiloxane polymers are used, then preferably, the degree of crosslinking is increased compared to formulations based on silsesquioxanes. These polymers and processes for spin-coating films containing such polymers are described in the commonly-owned, co-pending U.S. application Ser. No. _____, IBM Docket No. 920010250US1, filed on Apr. 16, 2002, entitled "Antireflective Si-Containing Compositions For Hardmask Layer," the contents of which are incorporated herein by reference in their entirety as if fully set forth.

[0040] Examples of SiO containing polymers include: poly(3-propanoloxypropyl)silsesquioxane, copolymer of 3-propanoloxypropylsilsesquioxane and phenylsilsesquioxane, blend of poly(hydroxybenzyl)silsesquioxane and poly(1-hydroxy-1-trifluoromethylethyl) silsesquioxane, copolymer of 1-hydroxy-1-trifluoromethylethylsilsesquioxane and p-Hydroxymethylbenzylsilsesquioxane.

[0041] A fourth layer may be interposed between the first layer (GeOHX layer) and the substrate. Examples of suitable fourth layers include, but are not limited to, a sacrificial hard mask layer, a capping layer and any combinations thereof. When the first layer is used as an anti-reflective coating alone, such a hard mask layer would be useful.

[0042] The substrate can be any substrate suitable in lithographic structures. Examples of suitable substrates include, but are not limited to, a semiconductor, a dielectric, a polymer, a glass, a metal, nonmetallic conductor, magnetic material and any combinations thereof. Examples of preferred materials for the substrate include, but are not limited to, Si, Ge, SiGe, polymers, oxide, nitride, metal and any combinations thereof.

[0043] The Ge, O, H, and X elements of the first layer (GeOHX layer) can be present in any atomic percent ratio. The preferred atomic percent (at. %) ranges for the Ge, O, H, and X elements are given as follows:—why do we need this paragraph?

[0044] For Ge, the atomic percent range is preferably from about 15 at. % to about 40 at. %, more preferably from about 17 at. % to about 35 at. %, and most preferably from about 20 at. % to about 30 at. %.

[0045] For O, the atomic percent range is preferably from about 15 at. % to about 85 at. %, more preferably from about 20 at. % to about 60 at. %, and most preferably from about 40 at. % to about 50 at. %.

[0046] For H, the atomic percent range is preferably from about 5 at. % to about 55 at. %, more preferably from about 10 at. % to about 45 at. %, and most preferably from about 15 at. % to about 30 at. %.

[0047] For X, the atomic percent range is preferably from about 0 at. % to about 50 at. %, more preferably from about 1 at. % to about 30 at. %, and most preferably from about 2 at. % to about 10 at. %.

[0048] The first layer has minimum to no interfacial interaction with the second layer and has good resolution down to 50 nm. The interface between first and second layers is substantially free of any undesirable chemical interactions, physical interactions, adhesion problems, and interfacial mixing.

[0049] The first layer has good etch selectivity to conventional energy photoactive materials, such as deep UV photoresists. Etch selectivities of the first layer to second layer range from about 10:1 to about 1:1, preferably are greater than about 1:1, and more preferably greater than about 2:1. The first layer is patternable by reactive ion etching in gas chemistry. Examples of suitable gasses include, but are not limited to oxygen, fluorine, chlorine, bromine, hydrogen and any combinations thereof. Example etch selectivities of 1.5:1 to 4:1 were obtained using a halogen and/or fluorocarbon-based chemistry in conjunction with a high-density plasma etcher. This will prevent the excessive photoresist loss observed in conventional ARC-open etches and allow thin resist process. The etch selectivity of the first layer to the substrate range from about 10:1 to about 1:1, preferably are greater than about 1:1, and more preferably greater than about 3:1.

[0050] The reflectance between the first layer and the second layer can be minimized by the use of the films of the present invention. Preferably the reflectance between the first and second layers is less than about 0.5%, and more preferably less than about 0.01%.

[0051] In one embodiment of the present invention, the optical, chemical, and physical properties of the first layer are not impacted or are impacted minimally by exposure to applied irradiation.

5

[0052] GeOHX films are water and aqueous base soluble and can be selectively removed from the structure without any substrate degradation or damage.

[0053] The first layer (GeOHX layer) can be deposited by various known methods. Examples of such methods include, but are not limited to, vapor deposition, plasma enhanced chemical vapor deposition, high density plasma, sputtering, ion beam, electron beam, laser assisted techniques, spin-coating and any combinations thereof.

plasma enhanced chemical vapor deposition (PECVD) techniques. In one type of technique the PECVD process is performed in a parallel plate reactor where the substrate is placed on one of the electrodes. In the following embodiment examples the substrate is placed on the powered electrode of a parallel plate PECVD reactor, therefore acquiring a negative bias.

[0056] Table 2 includes non-limiting exemplary embodiments of films deposited under the listed conditions.

TABLE 2

Example	Film/Layer Type	Precursor	Pressure in Reactor	Substrate T	Substrate Bias
1	GeOHX	tetramethylgermane at a flow of 5 sccm mixed with oxygen at a flow of 30 sccm	100 mtorr	60° C.	−150 V
2	GeOHX	tetramethylgermane at a flow of 10 sccm mixed with oxygen at a flow of 10 sccm	100 mtorr	60° C.	−50 V
3	GeOHX	tetramethylgermane at a flow of 5 sccm mixed with oxygen at a flow of 50 sccm	100 mtorr	60° C.	−250 V
4	GeOHX	tetramethylgermane at a flow of 10 sccm mixed with oxygen at a flow of 100 sccm	100 mtorr	60° C.	−150 V
5	GeOHX	tetramethylgermane at a flow of 10 sccm mixed with C_6H_{12} at a flow of 1.8 sccm	100 mtorr	60° C.	−150 V
6	GeOHX	tetramethylgermane at a flow of 10 sccm with tetramethylsilane at a flow of 10 sccm	100 mtorr	60° C.	−200 V
7	SiCOH	tetramethylsilane at a flow of 10 sccm mixed with oxygen at a flow of 2 sccm	200 mtorr	180° C.	−200 V
8	GeOHX	tetramethylgermane at a flow of 15 sccm mixed with oxygen at a flow of 2 sccm	200 mtorr	60° C.	−50 V
9	GeCHX	tetramethylgermane at a flow of 50 sccm with helium as a carrier gas at flow of 250 sccm	2 Torr	235° C.	Top electrode power = 400 W
10	GeOHX	tetramethylgermane at a flow of 50 sccm with helium as a carrier gas at flow of 250 sccm mixed with CO2 at a flow of 100 sccm	2 Torr	235° C.	Top electrode power = 400 W

[0054] The films of the first layer may be deposited from precursors. Examples of suitable precursors include, but are not limited to, germane, alkyl germane, alkoxy germane, acyloxy germane, aryl germane, cyclic germane, silicon containing precursor, oxygen containing precursor, nitrogen containing precursor, fluorine containing precursor, sulfur containing precursor, carbon dioxide, carbon monoxide, hydrogen and any combinations thereof.

[0055] In a preferred example, the films of the first layer are deposited by chemical vapor deposition (CVD), such as

[0057] Other examples of PECVD methods include a parallel plate PECVD reactor with the substrate positioned on the grounded electrode. The films can be deposited in conditions similar to those described in the previous 0 C. examples but at substrate temperatures up to 400° C., and in high density plasma type reactors under suitable chosen conditions. The films may also be deposited in a dual RF frequency PECVD reactor with the top RF power being from about 50 to about 2000 W and bottom RF power from about 0 to about 200 W.

[0058] It should be noted that by changing process parameters such as bias voltage, gas flow, pressure and deposition temperature, the optical constants of the film can be varied. In addition, the composition of the starting precursor as well as the introduction of oxygen, nitrogen, fluorine, silicon and carbon containing precursors also allows the tunability of these films.

[0059] The films of the first layer may also be deposited by spin-coating from a solgel derived process. For example, germanium, silicon, nitrogen, and fluorine containing precursors are hydrolyzed by acid in an organic solvent. This solution can then be spin applied onto the substrate followed by a bake to give the desired coating. The advantage of a spin-applied coating is its planarizing/gapfilling property, unlike CVD deposited films which are conformal. Many backend dual damascene structures contain via that need to be gapfilled and planarized prior to lithography. Complete gapfill of via structure is necessary to prevent the formation of voids in the via that would otherwise lead to structural defects after the etch process. In addition, planar films avoid thickness changes that could impact the lithography and the subsequent etch transfer. A planarizing coating procedure, therefore avoids the use of a chemical mechanical polishing step to planarize the surface prior to lithography. Thus, for integration schemes, such as the via first integration scheme for fabricating backend dual damascene structures, planarizing GeOHX films are desirable.

[0060] Examples of suitable germanium and silicon containing precursors include, but are not limited to, $Ge(OR)_4$, $Si(OR)_4$, $HGe(R^1)_3$, $HSi(R^1)_3$, $HGe(OR)_3$, $HSi(OR)_3$ and any combinations thereof, wherein R is selected from the group consisting of: methyl, ethyl, isopropyl, isobutyl, n-butyl and any combinations thereof, and wherein R^1 is a halogen.

[0061] The spin-coated films of the first layer may be highly cross-linked networks of Ge, O, and H, and optionally X. These films of the first layer can include functional groups represented by the formulas:
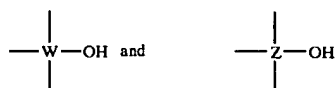
$$\overset{\displaystyle |}{\underset{\displaystyle |}{-W}}-O-\overset{\displaystyle |}{\underset{\displaystyle |}{Z}}-; \qquad \overset{\displaystyle |}{\underset{\displaystyle |}{-W}}-OH; \qquad \overset{\displaystyle |}{\underset{\displaystyle |}{-Z}}-OH$$
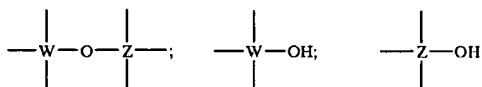
[0062] or any combinations thereof, wherein W and Z can be independently Ge, Si, N, and F.

[0063] The fewer

$$\overset{\displaystyle |}{\underset{\displaystyle |}{-W}}-OH \quad\text{and}\quad \overset{\displaystyle |}{\underset{\displaystyle |}{-Z}}-OH$$

[0064] functional groups, the higher the degree of cross-linking in the film. The

$$\overset{\displaystyle |}{\underset{\displaystyle |}{-W}}-OH \quad\text{and}\quad \overset{\displaystyle |}{\underset{\displaystyle |}{-Z}}-OH$$

[0065] functional groups are preferably present in a mole percent from about 1% to about 50%, more preferably in a

mole percent of less than about 10%, and most preferably in a mole percent of less than about 5%, based on the total film.

[0066] It should be noted that in addition to the first layer, a third layer, such as a cap layer including the RCOH material discussed above, may be deposited between the first layer and the second layer. This third layer may be CVD deposited or spin applied. After lithography, a pattern may be transferred into the third layer, followed by transfer of the pattern into the first layer. The second layer (energy photoactive layer) may be stripped off during any of these etch steps. The third layer may be consumed during the open of the dielectric layer (substrate). After completion of the etch process, the first layer may be stripped of by water or aqueous base.

[0067] The present invention further provides a method of making a lithographic structure which includes depositing on a surface of a substrate a first layer including a water and/or aqueous base soluble material which includes Ge, O, and H, and optionally X, wherein X is at least one of Si, N, and F; and depositing on the first layer a second layer which includes an energy photoactive material.

[0068] The depositing of the first layer may be repeated one or more times by depositing one or more of same or different layers which include Ge, O, and H, and optionally X, wherein X is at least one of Si, N, and F.

[0069] The index of refraction and the extinction coefficient of said first layer can be finely tuned to substantially match those of the substrate at a first interface between the first layer and the substrate and to substantially match those of the second layer at a second interface between the first layer and the second layer. This fine tuning is achieved as discussed above in relation to the lithographic structure.

[0070] A third layer may be deposited between the first layer and the second layer. The depositing of the third layer would occur after depositing of the first layer and before depositing of the second layer. The third layer may include an anti-reflective coating as discussed above with respect to the lithographic structure.

[0071] A fourth layer may be deposited between the first layer and the substrate. The depositing of the fourth layer would occur before depositing of the first layer. The fourth layer may include a sacrificial hard mask and/or capping layer as discussed above with respect to the lithographic structure.

[0072] The first layer can be deposited by any known technique. Suitable deposition techniques include, but are not limited to, vapor deposition, high density plasma, plasma enhanced chemical vapor deposition, sputtering, ion beam, electron beam, and laser assisted techniques.

[0073] The first layer may be deposited by plasma enhanced chemical vapor deposition from a precursor. Suitable precursors are discussed above in relation to the lithographic structure. The first layer may also be deposited by spin-coating as discussed above with respect to the lithographic structure.

[0074] The method of making a lithographic structure according to the present invention may further include the step of etching a pattern into the first layer after the step of depositing the second layer. The pattern can be formed by first forming a pattern in the second layer and thereafter

transferring the pattern to the first layer. The pattern may be transferred into the first layer by reactive ion etching in a plasma including a component selected from the group consisting of: fluorine, chlorine, bromine, fluorocarbon, oxygen, CO, CO2, nitrogen, helium, argon, hydrogen and any mixtures thereof. Subsequent to the transfer of the pattern into the first layer, the pattern may be transferred into the substrate material and then the first layer may be removed. The first layer may be removed by a water and/or aqueous base.

[0075] The following examples are given to illustrate the scope of the present invention. Because these examples are given for illustrative purposes only, the invention embodied therein should not be limited thereto.

EXAMPLE 1

[0076] FIG. 1 shows four examples of basic lithographic structures according to the present invention. FIG. 1(a) shows a lithographic structure according to the present invention. A substrate 10 has thereon a first layer 12 which includes a water and/or aqueous base soluble material which includes Ge, O, and H, and optionally X, wherein X is at least one of Si, N, and F (GeOHX layer). This GeOHX layer or first layer has thereon a second layer 14, which comprises an energy photoactive material. FIG. 1(b) shows a litho-graphic structure where the first layer 12 is made up of one or more of the same or different layers 16, 18, 20, and 22 which include Ge, O, and H, and optionally X, wherein X is at least one of Si, N, and F. It should be understood that the first layer 12 can have a single GeOHX layer or any number of GeOHX layers. FIG. 1(c) shows a lithographic structure where a third layer 24 is interposed between the first layer 12 and the second layer 14. FIG. 1(d) shows a lithographic structure where a fourth layer 26 is interposed between the first layer 12 and the substrate 10.

EXAMPLE 2

[0077] This example illustrates the removal of GeOHX materials in water and aqueous base solutions. The removal rates of GeOHX films were evaluated by measuring the dissolution rates using a quartz crystal microbalance (QCM). QCM is a standard technique used to determine the dissolution rate. Detailed description of this technique can be found in article by K. K. Kanazawa, W. D. Hinsberg *Rev. Sci. Instrum.* 60 (1989) 489-492. Dissolution rates in water and 0.26N tetramethylammoniunhydroxide (TMAH) aque-ous base solution have been evaluated. Dissolution rates of GeOHX films deposited under the conditions as described in the embodiments above using pressure of 100 mTorr, bias of −150V and varying TMGe to oxygen ratio from 0 to 10 have been measured. FIG. 2(a) shows the dissolution rates (A/sec) of GeOHX materials in water as a function of TMGe to O2 ratio. FIG. 2(b) shows the dissolution rates (A/sec) of GeOHX materials in 0.26N tetramethylammoniunhydroxide (TMAH) aqueous base solution as a function of TMGe to O2 ratio. It should be noted that solubility increases with the increase of oxygen content of the films. Substrate materials such as silicon oxide, silicon nitride and polysilicon are not soluble in water or aqueous base solution thus GeOHX can be selectively removed from the structure without any substrate degradation or damage.

EXAMPLE 3

[0078] The following example illustrates calculations for obtaining optimum optical constants and thickness of a

GeOHX film to be used as an ARC/Hardmask layer. Param-eters are optimized so as to reduce reflections at the ARC/resist interface. Computations are based on algorithms which use the Fresnel coefficients as found in standard textbooks such as Optics, by E. Hecht and A. Zajac, pub-lished in 1979 by Wiley, pages 312 and 313. These simu-lations can be extended to many different structures and they are not limited by the examples given below. The structure simulated in this example includes a Si substrate, GeOHX ARC-hard mask layer and photoresist. The parameters under investigation are the ARC-hard mask layer optical constants n and k and film thickness d. The acrylate-based 193 nm resist used in this study has n=1.72 and k=0.018 at 193 nm. The reflectance at the ARC/resist interface of thin ARCs of ~100 nm exhibits alternating maxima and minima, the positions of which depend on the n and k of the ARC/hardmask film. FIG. 3(a) shows the reflectance at the ARC/resist interface at 193 nm as a function of ARC/hardmask thickness for different values of n while keeping k constant at 0.5. High values of n and k, on the order of 2.0-2.1 and 0.5-0.6 respectively, are desirable for thin ARCs in order to minimize the thickness at the second minimum. While thin absorbing ARCs, operating at a reflectance minimum, can significantly suppress the reflectivity for a particular substrate; they are not as effective if the substrate thickness varies, or if there is significant topography on the wafer. Conversely, thick ARCs of ~300 nm, can provide better reflectivity control due to the small variation in reflectance caused by substrate reflectivity changes. FIG. 3(b) shows the reflectivity at the ARC/resist interface at 193 nm versus ARC thickness for different k values while keeping the value of n fixed. In this case, the extinction coefficient has a stronger impact on reflectance versus that of the index of refraction. The ARC film with n values in the range of 1.70 to 1.95 and k of ~0.20 to 0.22 will provide minimal thin film interference at this interface.

EXAMPLE 4

[0079] This example illustrates how to form layered (graded) GeOHX films to achieve a significant reduction in reflectivity at ARC/resist interface. In a multiple film first layer structure (FIG. 1(b)), the index of refraction (n) and the extinction coefficient (k) are graded throughout the first layer thickness to match the adjacent layers, if n and k of the first layer are perfectly matched to the adjacent layers, in principle, there should be no reflection at the interface between the first layer and the second layer. Variation in optical constants of GeOHX films was achieved by varying the precursor's composition, deposition conditions, as well as by doping films with different additives as described in the embodiments above. Table 1 shows the optical constants of different GeOHX materials. The index of refraction of GeOHX films was varied from about 1.58 to about 2.0 and the extinction coefficient from about 0.01 to 0.8 at various imaging wavelengths enabling a graded first layer structure.

[0080] We consider the example that shows significant reflectivity minimization by using a RCOH layer between a GeOHX and a resist. In this example, first, a 1000 A thick GeOHX film with n=1.845 and k=0.532 at 193 nm is deposited onto an Si substrate using process conditions as described in the deposition process in table 2, example 1 but using the substrate bias of −250V, and then, a 270 A thick SiCOH film with n=1.8 and k=0.22 is deposited using a process condition as described in U.S. Pat. Nos. 6,316,167

and 6,514,667. FIG. 4 represents a reflectance at the interface between the ARC/hardmask and the resist at 193 nm for this structure. A significant reflectivity reduction (about 0.0001), as well as insensitivity to hardmask thickness variation verses a single layer ARC/hardmask can be achieved by using tunable (layered) hardmask process which are show in FIG. 4.

EXAMPLE 5

[0081] The following example is given to demonstrate the performance of GeOHX films as an ARC/hardmask layer for advanced resist process. The following example also demonstrates the formation of device features of 0.2 μm (micron not mm) and below using a GeOHX vapor deposited ARC/hardmask material. A GeOHX film was deposited as described in the deposition process described in Table 2, example 1 onto 8" wafer. A 248 nm resist (Shipley UV82 resist) was spun on the top of the GeOHX film and post-apply baked. Then the resist was exposed to 248 nm radiation at a dose of about 28 mJ/cm2 using ASML microstepper and post-exposed baked. Then the resist is developed in LDD26W Shipley developer. FIG. 5(a) shows cross-sectional SEM image of 150 nm L/S developed resist profiles on a PECVD deposited single layer GeOHX ARC/hardmask film and shows no residue at the resist/GeOHX film interface. A resist is about 6,000 Angstroms and the GeOHX film thickness is about 2,400 Angstroms.

[0082] The feasibility of using graded (layered) GeOHX ARC/hardmask for 193 nm lithography was also demonstrated. Graded (layered) GeOHX ARC/hardmask material as described in Example 4 was deposited onto 8" wafer. Commercial 193 nm resist was spun on top, followed by 193 nm imaging and development as described above. FIG. 5(b) shows cross-sectional SEM image of sub-150 nm L/S patterns over graded GeOHX structure.

EXAMPLE 6

[0083] This example illustrates the etch selectivity of GeOHX materials to conventional deep UV and 193 nm photoresists. Having the appropriate etch selectivity to resist is among the most critical requirements of ARC/hardmask materials. Current organic ARCs have elemental chemical composition very similar to photoresists. This leads to little differentiation between the etch characteristics of these two material sets, resulting in a significant portion of the resist being consumed during the ARC open process. Thus, less resist remains for substrate etching. Furthermore, the organic ARC offers minimal etch-resistance during subsequent dielectric etch. For high-resolution lithography it is important to design ARC materials that will provide good etch selectivity to resist, as well as provide hardmask characteristics for the subsequent etch transfer. FIG. 6 shows the blanket etch rates of a GeOHX material compared with those of 248 and 193 nm resist films in a fluorocarbon based chemistry on a high-density plasma etch tool. The blanket selectivities of GeOHX material to 193 nm resist is about ~3.7:1 and to 248 nm resist is about ~5.5:1. This selectivity of more then 3 to 1 compares very favorably with the selectivity values of conventional organic ARC to resist of ~0.7.

EXAMPLE 7

[0084] The following example illustrates how the water and/or aqueous base soluble GeOHX ARC/hardmask material can be used and easily removed in a dual damascene process. Requirements to improve IC performance, such as faster clock speeds and lower power consumption, require the use of low-k materials for interconnects in chip manufacturing. However, the integration of low-k materials in a dual damascene process presents several technical challenges. Damage-free removal process of sacrificial masking materials after the patterning is complete is one of the key challenges (P. G. Clark et. al., Semiconductor International August, 2003 p 46-52).

[0085] FIG. 7 shows a diagram of the process flow for the dual damascene process. Incoming structure having an insulator substrate 30, such as low k or ultra low-k dielectric materials, deposited onto an etch stop substrate 32 containing a planarized metal line, and via is etched into the insulator by RIE process and then, capped with a cap material 34 to preserve the dielectric constant as shown in FIG. 7 (a). A first layer 36 (water soluble GeOHX ARC/hardmask material) as described in previous examples is deposited over and the second layer 38 (photoresist) is spun on top, exposed and developed. FIG. 7(b) shows the diagram of Mx+1 level lithography. FIG. 7(c) shows the result of the first layer 36 being etched by fluorocarbon or halogen plasma, followed by a pattern transferred into the dielectric through the first layer 36 and cap material 34 (FIG. 6 (d)). The second layer 38 and partially first layer 36 are also consumed during the M_{x+1} open. FIG. 6(e) shows the result of the remaining first layer 36 being easily removed in water solution selective and damage-free to the low-k material 30 and etch-stop material 32. Water is known not to affect the dielectric properties of both low-k and etch-stop materials, and therefore quick removal of the ARC/HM material by a water-based strip process is highly desirable.

[0086] While the films in the examples above were prepared by plasma enhanced chemical vapor deposition (PECVD), similar films can be prepared by any radiation-assisted technique or by spin-coating. Such radiation-assisted techniques include, but are not limited to, PECVD, high density plasma (HDP), sputtering, ion beam, electron beam, and laser assisted techniques.

EXAMPLE 8

[0087] FIG. 8 shows an example of how a planarizing, spin-coated GeOHX material can be used. FIG. 8(a) shows an incoming structure having an insulator substrate 40, such as low k or ultra low-k dielectric materials, deposited onto an etch stop substrate 42, via is etched into the insulator, and the insulator is capped with a cap material 44. FIG. 8(b) shows a spin applied GeOHX material 46 that forms a planarizing layer and an RCOH layer 48. FIG. 8(c) shows the diagram of Mx+1 level lithography. The resist 50 has been applied, exposed, and developed. FIG. 8(d) shows the ARC/Hardmask open and FIG. 8(e) shows the Mx+1 open. The pattern is thus transferred to the insulator substrate. The resist 50 and the RCOH layer 48 have also been removed. FIG. 8(f) shows the results of the GeOHX material removal in water and/or aqueous base.

[0088] The present invention has been described with particular reference to the preferred embodiments. It should be understood that the foregoing descriptions and examples are only illustrative of the invention. Various alternatives and modifications thereof can be devised by those skilled in

the art without departing from the spirit and scope of the present invention. Accordingly, the present invention is intended to embrace all such alternatives, modifications, and variations that fall within the scope of the appended claims.

What is claimed is:

1. A multilayer lithographic structure comprising a substrate, having on a major surface thereof a first layer which comprises a water and/or aqueous base soluble material comprising Ge, O, and H, and optionally X, wherein X is at least one of Si, N, and F; and disposed on said first layer a second layer which comprises an energy photoactive material.

2. The lithographic structure of claim 1, wherein said substrate is selected from the group consisting of: a semiconductor, a dielectric, a polymer, a glass, a metal, nonmetallic conductor, magnetic material and any combinations thereof.

3. The lithographic structure of claim 1, wherein said energy photoactive material is selected from the group consisting of: compositions which are photosensitive to 248 nm, 193 nm, 157 nm, 126 nm and extreme ultraviolet radiation, electron beam, ion beam, x-ray irradiation and any combinations thereof.

4. The lithographic structure of claim 1, wherein said first layer comprises one or more of same or different layers comprising Ge, O, and H, and optionally X, wherein X is at least one of Si, N, and F.

5. The lithographic structure of claim 4, wherein said first layer has an index of refraction and an extinction coefficient that are finely tuned to substantially match those of said substrate at a first interface between said first layer and said substrate and to substantially match those of said second layer at a second interface between said first layer and said second layer.
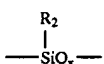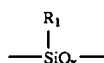
6. The lithographic structure of claim 5, wherein said index of refraction is tunable between from about 1.4 to about 2.6 and wherein said extinction coefficient is tunable from about 0.01 to about 0.78.

7. The lithographic structure of claim 1, wherein said first layer functions as a hardmask layer, an anti-reflection layer, or a combined hardmask/anti-reflection layer.
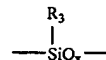
8. The lithographic structure of claim 1, wherein a third layer comprising an anti-reflective coating is interposed between said first layer and said second layer.

9. The lithographic structure of claim 8, wherein said anti-reflective coating comprises R, C, O, and H, wherein R is selected from the group consisting of: Si, Ge, Ti and any combinations thereof.

10. The lithographic structure of claim 9, wherein said anti-reflective coating comprises a polymer comprising one or more functional groups selected from the group consisting of:

$$
\begin{array}{c}
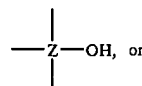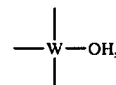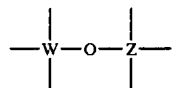R_1 \\
| \\
-\!\!-\mathrm{SiO}_x-\!\!-
\end{array} \tag{I}
$$

$$
\begin{array}{c}
R_2 \\
| \\
-\!\!-\mathrm{SiO}_x-\!\!-
\end{array} \tag{II}
$$

-continued

$$
\begin{array}{c}
R_3 \\
| \\
-\!\!-\mathrm{SiO}_x-\!\!-
\end{array} \tag{III}
$$

wherein x is from about 1 to about 1.5; R_1 comprises a chromophore moiety; R_2 comprises a transparent moiety; and R_3 comprises a reactive site for reaction with a crosslinking compound.

11. The lithographic structure of claim 1, wherein a fourth layer comprising a sacrificial hard mask and/or a capping layer is interposed between said first layer and said substrate.

12. The lithographic structure of claim 1, wherein said first layer is deposited by a technique selected from the group consisting of: vapor deposition, plasma enhanced chemical vapor deposition, high density plasma, sputtering, ion beam, electron beam, laser assisted techniques and any combinations thereof.

13. The lithographic structure of claim 1, wherein said first layer is deposited from a precursor selected from the group consisting of: germane, alkyl germane, alkoxy germane, acyloxy germane, aryl germane, cyclic germane, silicon containing precursor, oxygen containing precursor, nitrogen containing precursor, fluorine containing precursor, sulfur containing precursor, carbon dioxide, carbon monoxide, hydrogen and any combinations thereof.

14. The lithographic structure of claim 1, wherein said first layer comprises a material which comprises a functional group represented by the formula:

$$
\begin{array}{c}
| \qquad\quad | \\
-\!\!-\mathrm{W}-\!\!\mathrm{O}-\!\!\mathrm{Z}-\!\!-, \\
| \qquad\quad |
\end{array} \tag{a}
$$

$$
\begin{array}{c}
| \\
-\!\!-\mathrm{W}-\!\!\mathrm{OH}, \\
|
\end{array} \tag{b}
$$

$$
\begin{array}{c}
| \\
-\!\!-\mathrm{Z}-\!\!\mathrm{OH}, \text{ or} \\
|
\end{array} \tag{c}
$$

d) any combinations thereof,

wherein W and Z are independently selected from the group consisting of: Ge, Si, N, and F.

15. The lithographic structure of claim 14, wherein said functional group b) and c) are present in a mole percent of less than about 5%.

16. The lithographic structure of claim 14, wherein said first layer is deposited by spin coating.

17. The lithographic structure of claim 14, wherein said first layer is deposited from a precursor selected from the group consisting of: $Ge(OR)_4$, $Si(OR)_4$, $HGe(R^1)_3$, $HSi(R^1)_3$, $HGe(OR)_3$, $HSi(OR)_3$ and any combinations thereof, wherein R is selected from the group consisting of: methyl, ethyl, isopropyl, isobutyl, n-butyl and any combinations thereof, and wherein R^1 is a halogen.

18. The lithographic structure of claim 1, wherein said first layer is patternable by reactive ion etching in a gas chemistry with an etch selectivity to said substrate that is greater than about 1:1.

19. The lithographic structure of claim 1, wherein said first layer comprises by atomic %: Ge from about 15 at. % to about 40 at. %; O from about 15 at. % to about 85 at. %; H from about 5 at. % to about 55 at. %; X from about 0 at. % to about 50 at. %.

20. The lithographic structure of claim 1, wherein the optical, chemical, and physical properties of said first layer are not impacted by exposure to an irradiation applied to said lithographic structure.

21. The lithographic structure of claim 1, wherein said second layer is a chemically amplified resist.

22. The lithographic structure of claim 1, wherein said second layer has a thickness from about 250 A to about 6000 A.

23. The lithographic structure of claim 1, wherein an etch selectivity of said second layer to said first layer is greater than about 1:1.

24. The lithographic structure of claim 1, wherein said lithographic structure is substantially free of interfacial interaction of said first layer and said second layer.

25. The lithographic structure of claim 1, wherein said lithographic structure has a reflectance at the interface between said first and second layers of less than about 0.01%.

26. A method of making a lithographic structure comprising:

depositing on a surface of a substrate a first layer which comprises a water and/or aqueous base soluble material comprising Ge, O, and H, and optionally X, wherein X is at least one of Si, N, and F; and

depositing on said first layer a second layer comprising an energy photoactive material.

27. The method of claim 26, wherein said depositing of said first layer is repeated one or more times by depositing one or more of same or different layers comprising Ge, O, and H, and optionally X, wherein X is at least one of Si, N, and F.

28. The method of claim 27, wherein the index of refraction and the extinction coefficient of said first layer are finely tuned to substantially match those of said substrate at a first interface between said first layer and said substrate and to substantially match those of said second layer at a second interface between said first layer and said second layer.

29. The method of claim 26, further comprising depositing a third layer comprising an anti-reflective coating between said first layer and said second layer.

30. The method of claim 29, wherein said anti-reflective coating comprises R, C, O, and H, wherein R is selected from the group consisting of: Si, Ge, Ti and any combinations thereof.

31. The method of claim 26, further comprising depositing a fourth layer comprising a sacrificial hard mask and/or capping layer between said first layer and said substrate.

32. The method of claim 26, wherein said first layer is deposited by a technique selected from the group consisting of: vapor deposition, high density plasma, plasma enhanced chemical vapor deposition, sputtering, ion beam, electron beam, and laser assisted techniques.

33. The method of claim 26, wherein said first layer is deposited by plasma enhanced chemical vapor deposition from a precursor selected from the group consisting of: germane, alkyl germane, alkoxy germane, acyloxy germane, aryl germane, cyclic germane, silicon containing precursor, oxygen containing precursor, nitrogen containing precursor, fluorine containing precursor, sulfur containing precursor, carbon dioxide, carbon monoxide, hydrogen and any combinations thereof.

34. The method of claim 26, wherein said first layer is deposited by spin-coating.

35. The method of claim 26, wherein said first layer is deposited from a precursor selected from the group consisting of: $Ge(OR)_4$, $Si(OR)_4$, $HGe(R^1)_3$, $HSi(R^1)_3$, $HGe(OR)_3$, $HSi(OR)_3$ and any combinations thereof, wherein R is selected from the group consisting of: methyl, ethyl, isopropyl, isobutyl, n-butyl and any combinations thereof, and wherein R^1 is a halogen.

36. The method of claim 26, further comprising etching a pattern into said first layer.

37. The method of claim 36, wherein said pattern is formed by first forming a pattern in said second layer and thereafter transferring said pattern to said first layer.

38. The method of claim 37, wherein said pattern is transferred into said first layer by reactive ion etching in a plasma comprising a component selected from the group consisting of: fluorine, chlorine, bromine, fluorocarbon, oxygen, CO, CO2, nitrogen, helium, argon, hydrogen and any mixtures thereof

39. The method of claim 26, further comprising removing said first layer by water and/or aqueous base.

40. A film for a lithographic structure comprising Ge, O, and H, and optionally X, wherein X is at least one of Si, N, and F, and wherein said film is water and/or aqueous base soluble.

* * * * *

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(54) **WET DEVELOPABLE HARD MASK IN CONJUNCTION WITH THIN PHOTORESIST FOR MICRO PHOTOLITHOGRAPHY**

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(57) **ABSTRACT**

A novel process for using a hard mask or protective layer in conjunction with an extremely thin photoresist is provided. In this process, a thin film of the protective layer is coated on the surface of a substrate that is to be selectively modified by reactive ion etch (RIE). The protective layer is photo-sensitive and anti-reflective. An extremely thin photoresist layer is coated on top of the protective layer. The stack of the films is selectively exposed to actinic radiation at a wavelength determined by the sensitivities of the protective layer and photoresist layer. The latent images on the photoresist and protective layers resulting from the exposure are developed with a common alkaline developer. The three dimensional patterns of photoresist and underlying protective layer are formed simultaneously by the single exposure and single development. When the underlying substrate is etched by RIE, the protective layer is the masking layer, not the photoresist.
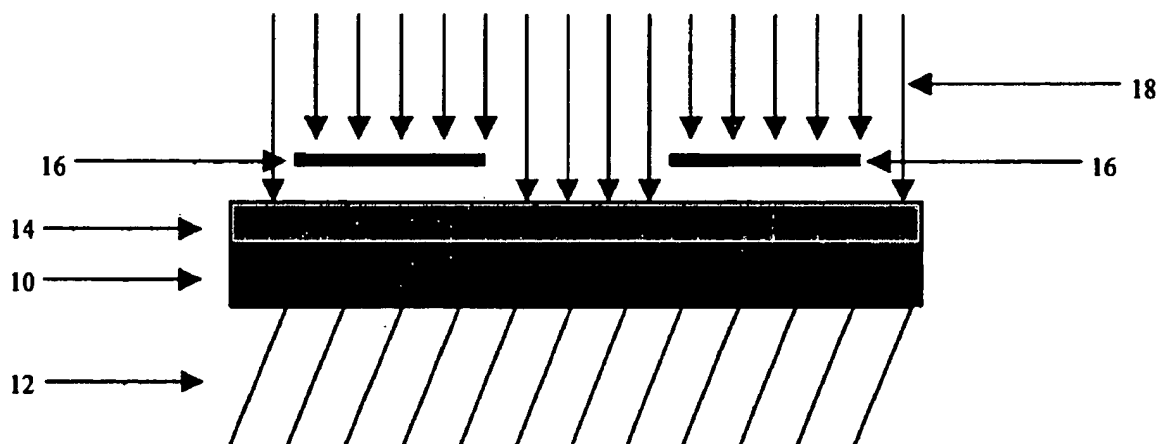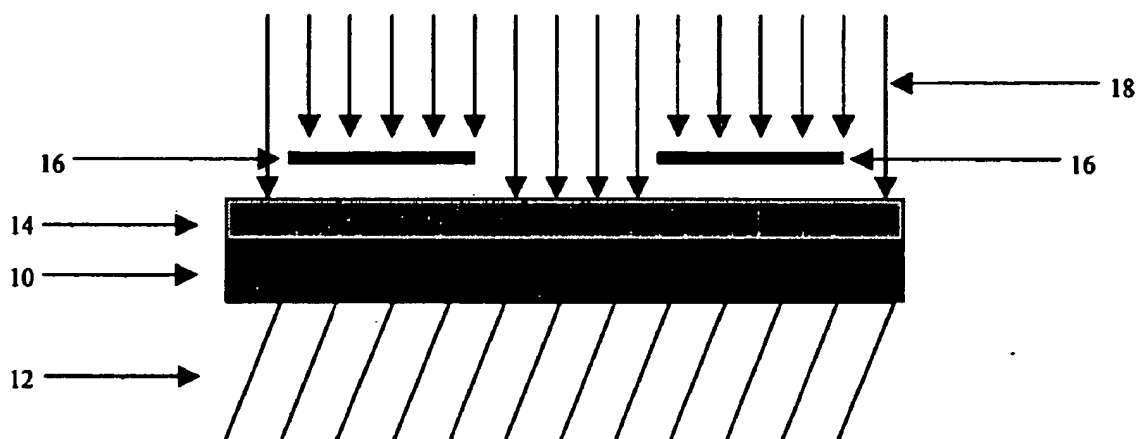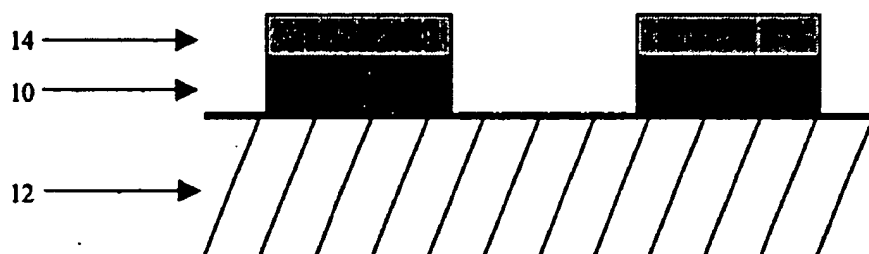
14

10

12

Figure 1a

18

16
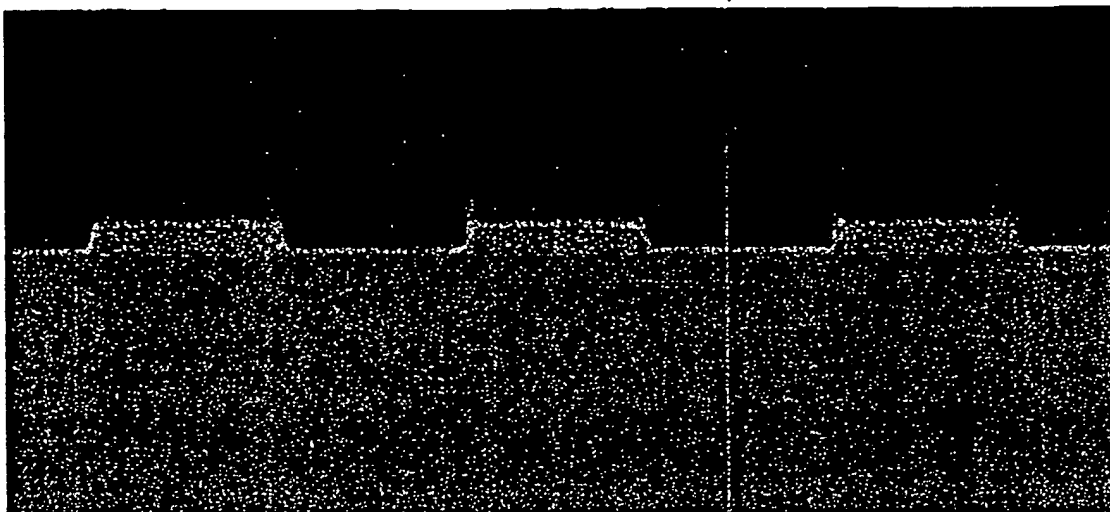
16

14

10

12

Figure 1b

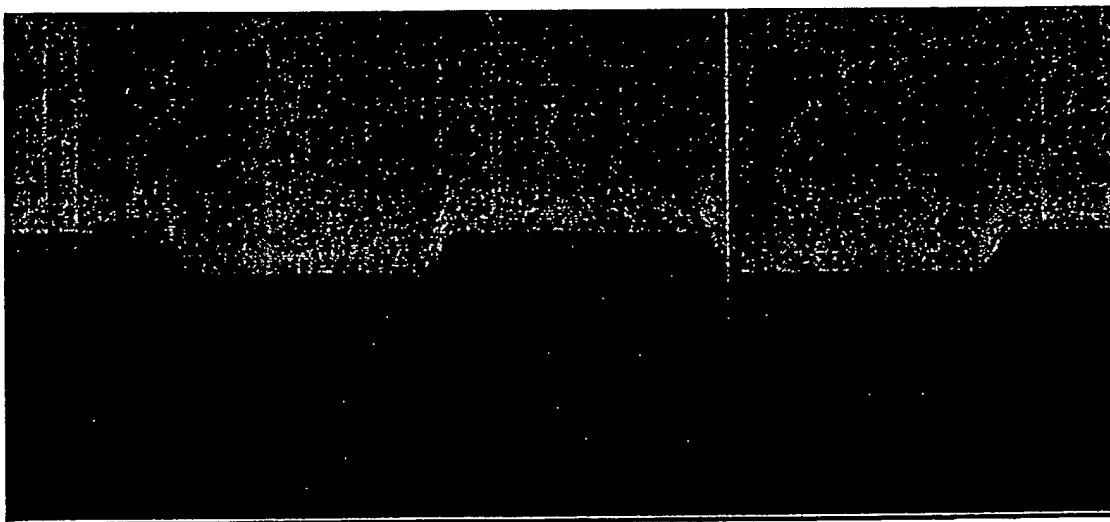14

10

12

Figure 1c

10

12

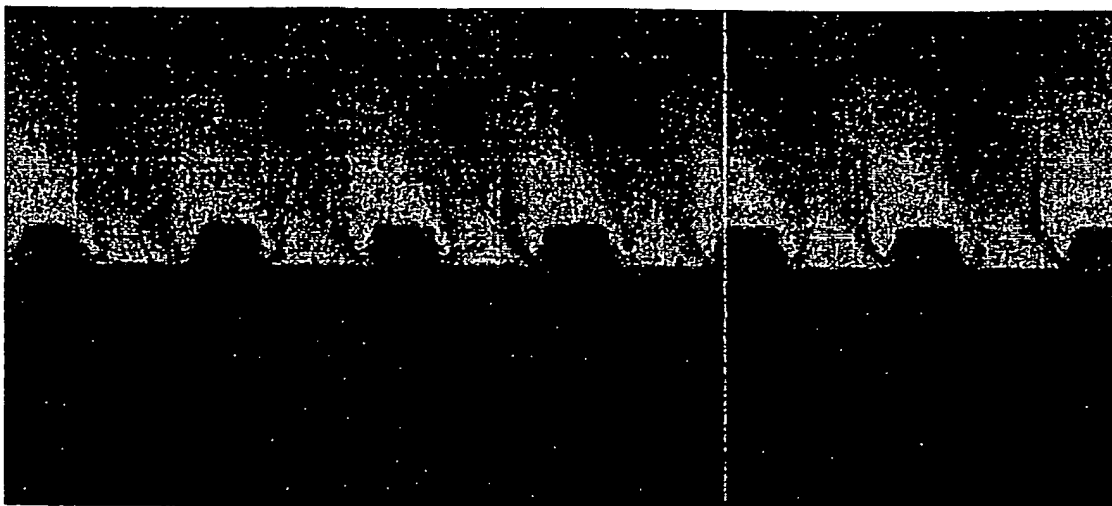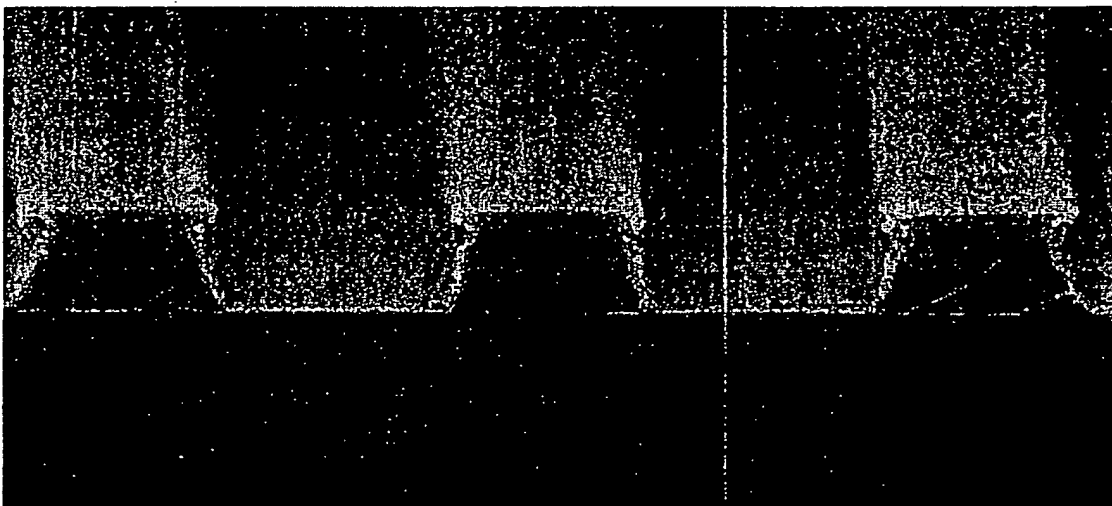Figure 1d
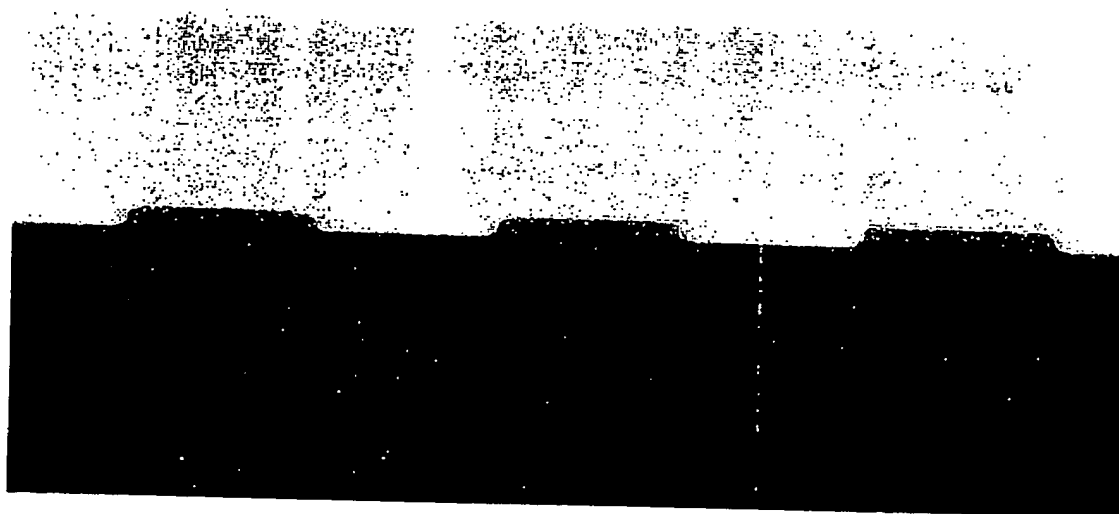
Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

WET DEVELOPABLE HARD MASK IN CONJUNCTION WITH THIN PHOTORESIST FOR MICRO PHOTOLITHOGRAPHY

RELATED APPLICATIONS

[0001] This application claims the priority benefit of a provisional application entitled ENHANCED MICROPHOTOLITHOGRAPHY PERFORMANCE WITH THIN PHOTORESISTS AND WET-DEVELOPABLE, PHOTOSENSITIVE ANTI-REFLECTIVE HARD MASKS, Ser. No. 60/477,580, filed Jun. 11, 2003, incorporated by reference herein.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention is broadly directed towards new methods of forming microelectronic structures where extremely thin photoresists layers can be utilized.

[0004] 2. Description of the Prior Art

[0005] When a photoresist is used to generate patterns by light exposure, Rayleigh's laws can be used to define the pattern resolution and depth of focus (DOF):

$$\text{Resolution}=k_1 \lambda/NA; \text{ and}$$

$$DOF=k_2 \lambda/NA^2,$$

[0006] where λ is the irradiation wavelength, NA is the numerical aperture of the exposure tool, and k_1 and k_2 are constants for a given process. Rayleigh's theory indicates that an exposure tool with short wavelength and large numerical aperture will produce better pattern resolution. This principle is why the microelectronics industry has been progressively moving toward short exposure wavelengths. However, Rayleigh's law also shows that enhancing resolution causes the DOF to decrease.

[0007] The use of a thin photoresist decreases the value of k_1 and increases the value of k_2, which results in better resolution and a large DOF. As a result, extensive research has been conducted in an attempt to reduce photoresist thicknesses in photolithographic processes. Due to the different etch selectivities (with the different etch chemistries) of the hard mask over the photoresist, and of the hard mask over the substrate, the most effective way to reduce photoresist thickness is by introducing a hard mask into the etch stack.

[0008] Silicon nitride, silicon oxynitride, silicon nitride/oxide, silicon oxide/nitride, transition metals, amorphous silicon, and metal/oxide hard masks have been introduced into the etch stack to attempt to decrease the necessary photoresist thickness in photolithographic processes. The hard mask-to-photoresist etch selectivity for a given thickness of the hard mask determines how thin the photoresist can be. Unfortunately, organic photoresists etch relatively fast under common hard mask plasma etch chemistries and conditions. Thus, the photoresist thickness is still substantial even with multiple hard masks.

[0009] A multilayer or composite photoresist process has also been attempted. In this process, a somewhat thinner photoresist layer is formed on a substrate and is subsequently exposed and developed to pattern the photoresist. The process is repeated until the desired number of photo-resist layers are accumulated. The thinner each layer is, the more layers that must be processed for a specific final thickness. The drawbacks of this process are as clear as the advantages. In particular, the procedure is cumbersome, and the patterns for each photoresist layer must be perfectly aligned.

[0010] There is a need for a process that minimizes or even eliminates these problems.

SUMMARY OF THE INVENTION

[0011] The advanced hard mask and process of the present invention minimize, and more preferably eliminate, the problems described above. In one aspect, the invention is broadly concerned with a method of forming structures to be used in various microelectronic applications such as photolithographic processes for integrated circuit (IC) fabrication and microelectromechanical systems (MEMS) applications.

[0012] In more detail, the methods comprise initially applying via any known method (e.g., spin coating) a protective or hard mask layer to a substrate. Exemplary substrates include those selected from the group consisting of silicon, polysilicon, silicon oxide, silicon nitride, silicon oxynitride, gallium arsenide, aluminum, tungsten, titanium, titanium-tungsten, nickel, copper, and gold substrates. The protective layer may be applied directly to the substrate surface, or to one or more intermediate layers (e.g., planarizing layers, additional hard mask layer(s)) that are first applied to the substrate surface. Regardless, the substrate can be a planar surface, or it can include topography (via holes, contact holes, raised features, etc.).

[0013] After the protective layer is applied, it is preferably subjected to a curing step by heating at a temperature of from about 130-250° C., and more preferably from about 180-210° C. The thickness of the protective layer after baking is preferably from about 20-150 nm, more preferably from about 40-100 nm, and even more preferably from about 40-80 nm.

[0014] The protective layer is preferably wet developable. That is, the cured composition can be removed with conventional aqueous developers such as tetramethyl ammonium hydroxide (TMAH) and KOH developers. Some of these developers are commercialized under the tradenames MF-319 (available from Shipley, Mass.), MF-320 (available from Shipley), and NMD3 (available from TOK, Japan) developers. At least about 95%, and preferably at least about 99% of the inventive coatings will be removed by a base developer such as tetramethyl ammonium hydroxide and KOH developers.

[0015] Wet-developable layers in photolithographic processes are prone to pattern undercut due to the isotropic nature of wet development. In the present invention, the undercut issue is resolved by making the protective layer photosensitive. Thus, a pattern can be defined in the protective layer when it is exposed to at least about 1 mJ/cm^2.

[0016] The protective layer preferably possesses light absorbing properties. Specifically, the protective layer used in the inventive methods will have a k value (the imaginary component of the complex index of refraction) of at least about 0, preferably at least about 0.1, and more preferably from about 0.2-0.5, and an n value (the real component of the complex index of refraction) of at least about 1.2, and

preferably from about 1.6-1.8. These values can be obtained at a wide range of wavelengths, including wavelengths of less than about 500 nm (e.g., 436 nm, 365 nm, 248 nm, 193 nm, 157 nm, 13 nm, 11 nm, 4 nm, and X-ray).

[0017] The protective layer should also have a high etch selectivity over the substrate to provide an adequate plasma barrier. This is because the photoresist layer in this process is used for patterning the protective layer by exposure and wet development only, whereas the photoresist functions as a plasma-etch barrier as well in conventional processes. Thus, the etch selectivity of the protective layer over the substrate (e.g., polysilicon) will be at least about 1, preferably at least about 5, and more preferably from about 10-200, when chlorine or HBr is used as the etchant. Furthermore, the etch selectivity of the protective layer over the photoresist (e.g., a 193-nm photoresist) will be at least about 1, preferably at least about 5, and more preferably from about 10-100, when chlorine or oxygen is used as the etchant. The protective layer should etch at a rate of less than about 5 nm/second, and more preferably from about 0.02-1 nm/second, when chlorine or HBr is the etchant.

[0018] After the protective layer is applied, a photoresist can then be applied to the protective layer followed by baking at a temperature of from about 90-180° C., and more preferably from about 90-1 30° C. Advantageously, the photoresist can be used as a much thinner layer than was the case with prior art processes. The photoresist thickness after baking will be less than about 150 nm, preferably from about 20-100 nm, and even more preferably from about 20-60 nm. This small photoresist thickness is possible due to the presence of the protective layer having the properties defined above. As a result, a photoresist composition having a solids content (prior to baking) of less than about 5% by weight, and more preferably from about 1.5-3.0% by weight, can be used. Such a photoresist can be specifically prepared for this purpose, or a commercially available photoresist can be diluted until the desired solids content is achieved.

[0019] The photoresist can then be exposed and developed. Following the methods of the invention will yield precursor structures for line/space, dual damascene, and other microlithographic processes which have the foregoing desirable properties.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] FIGS. 1a-1d are schematic drawings depicting a structure formed by the inventive process;

[0021] FIG. 2 is a scanning electron microscope (SEM) photograph showing the cross-sectional view of a wafer prepared according to the inventive process;

[0022] FIG. 3 is an SEM image showing a cross-sectional view of a wafer prepared according to the invention with the thinnest photoresist;

[0023] FIG. 4 is an SEM image showing a cross-sectional view of a wafer prepared according to the invention with 248-nm exposure;

[0024] FIG. 5 is an SEM image showing a cross-sectional view of poly silicon line/space patterns fabricated according to the invention; and

[0025] FIG. 6 is an SEM image showing a cross-sectional view of the protective layer-line/space patterns after ion implantation.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0026] In more detail, FIGS. 1a-1d illustrate the stack of layers for the inventive photolithographic process. Referring to FIG. 1a, a photosensitive and anti-reflective hard mask or protective layer 10 is spin coated onto the substrate 12 at a thickness of from about 20-150 nm, depending upon its etch selectivity over the substrate, substrate etch depth, and its optical properties (e.g., refractive index, extinction coefficient). The protective layer is preferably subsequently cured by baking on a hot plate. A thin photoresist layer 14, positive-working or negative-working depending on the tone of the underlying protective layer, is then spin coated on top of the protective layer at a thicknesses described above.

[0027] In FIG. 1b, patterns on a photomask 16 are transferred onto the thin photoresist layer 14 by irradiation 18. As demonstrated in FIG. 1c, the patterns are then transferred to the protective layer 10 by development (preferably simultaneously) with the photoresist layer 14 by an alkaline developer. Finally, the substrate 12 is plasma etched through the patterned protective layer 14 (FIG. 1d).

[0028] The photolithographic process can be used with any microelectronic substrates. Furthermore, the process can be used in MEMS applications or in conjunction with organic dielectric layers, planarization layer, and metal layers to be etched for patterns or structures through the wet-developable protective layer and thin resist.

[0029] The protective layer-thin photoresist process can be used in the ion implant process for IC fabrication as well. The stack of layers in the ion implant process is the same as demonstrated in FIG. 1a. When the substrate is implanted with boron, phosphorous, arsenic, or any other elements, the patterned protective layer serves as an ion barrier.

[0030] In one preferred embodiment, the protective layer may comprise any combination of a polymeric metal alkoxide, polymer binder, polyols, chromophore (e.g., cyano acrylate, 9-anthracenecarboxylic acid, and 4-hydroxybenzoic acid), photo acid generator (PAG, e.g., TAZ-108™), photo initiator (e.g., Irgacure 184™), and organic solvents. Some particularly preferred compositions are disclosed in U.S. patent application Ser. No. 10/180,625, filed Jun. 25, 2002, and incorporated by reference herein.

[0031] In one embodiment, preferred protective layer compositions comprise polymers that include recurring units having the formula
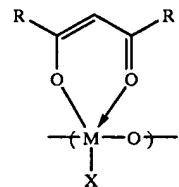
[0032] wherein X is selected from the group consisting of light-attenuating moieties and polyols, M is a metal, and each R is individually selected from the group consisting of hydrogen, alkyls (preferably C_1-C_8), aryls, alkoxys, and phenoxys. The most preferred R groups are —CH_3 and —OC_2H_5.

[0033] The most preferred metals are Ti, Zr, Si, and/or Al. It is also preferred that the light-attenuating moiety include a functional group for coordinating with the metal atom of the polymeric metal alkoxide. Such functional groups include carbonyl, alcohol, and phenol groups. Furthermore, the moiety (i.e., X) is preferably present in the polymer at a level of from about 2-50% by weight, and more preferably from about 2-25% by weight, based upon the total weight of the polymer taken as 100% by weight. Suitable light-attenuating moieties include those selected from the group consisting of moieties oftrimethylol ethoxylate, 4-hydroxy-benzaldehyde, and 2-cyano-3-(4-hydroxyphenyl)-acrylic acid ethyl ester.

[0034] The preferred composition is formed by simply dispersing or dissolving the polymers in a suitable solvent system, preferably at ambient conditions and for a sufficient amount of time to form a substantially homogeneous dispersion. The polymer should be present in the composition at a level of 2-50% by weight, more preferably from about 5-30% by weight, and more preferably from about 7-15% by weight, based upon the total weight of solids in the composition taken as 100% by weight.

[0035] Preferred solvent systems include a solvent selected from the group consisting of propylene glycol methyl ether acetate (PGMEA), propylene glycol methyl ether (PGME), propylene glycol n-propyl ether (PnP), ethyl lactate, and mixtures thereof. Preferably, the solvent system has a boiling point of from about 50-250° C., and more preferably from about 100-175° C. The solvent system should be utilized at a level of from about 70-95% by weight, and preferably from about 80-90% by weight, based upon the total weight ofthe solids in the composition taken as 100% by weight.

[0036] Any additional ingredients are also preferably dispersed in the solvent system along with the polymer. One such preferred additional ingredient is a second polymer or polymer binder such as those selected from the group consisting of epoxy novolac resins (e.g., Epon 164®, available from Araldite), acrylates (e.g., poly(glycidyl methacry-late)), polymerized aminoplasts (e.g., Cymel® products available from Cytec Industries), glycourils (e.g., Powder-link® products available from Cytec Industries), vinyl ethers, and mixtures thereof. The weight average molecular weight of this additional polymer is preferably from about 1,000-50,000 Daltons, and more preferably from about 5,000-25,000 Daltons. In embodiments where an additional polymer is utilized, the composition should comprise from about 1-50% by weight of this additional polymer, and more preferably from about 5-25% by weight, based upon. the total weight of the solids in the composition taken as 100% by weight.

[0037] It will be appreciated that a number of other optional ingredients can be included in the protective layer composition as well. Typical optional ingredients include light attenuating compounds, surfactants, catalysts, crosslinkers, and adhesion promoters.

[0038] With respect to the preferred photoresists, commercially available photoresists do not form a 20- to 150-nm thick film. Rather, they must be thinned in order to meet the above-described requirements. Thinning of the photoresist is preferably accomplished with organic solvents such as ethyl lactate, PGME, PnP, PGMEA, and/or 2-heptanone in sufficient amounts to obtain the solids contents described herein.

[0039] The thin photoresist provides a number of important advantages to the photolithographic process. First, there are no outstanding photoresist patterns in the entire process. Dry etch masking is no longer required for the photoresist, making the photoresist more of a photosensitive layer rather than a photoresist. Second, the photoresist layer is so thin that transparency becomes less of a problem. Third, due to the extraordinarily thin photoresist, this invention opens an opportunity to replace the ever troubling chemically amplified photoresist with non-chemically amplified photoresists for the photolithography process of KrF or shorter wavelengths. Fourth, chances for the protective layer and photoresist patterns to collapse are significantly reduced, if not completely eliminated, due to the low aspect ratios and the excellent adhesion of the protective layers to substrates. Fifth, the thinness of the photoresist will inevitably improve the pattern resolution. Sixth, the exposure focus offset has less impact on a thin photoresist than on a thick one. Critical dimension (CD) variation of the protective layer patterns due to different DOF is less significant due to the thin photoresist.

EXAMPLES

[0040] The following examples set forth preferred methods in accordance with the invention. It is to be understood, however, that these examples are provided by way of illustration and nothing therein should be taken as a limitation upon the overall scope of the invention.

Example 1

Protective Layer Formulations

[0041] 1. Preparation of Protective Layer Formulation 1

[0042] The ingredients used in this part are set forth in Table 1 below. The diketone ligand (ethyl acetoacetate), chromophore (cyano acrylate), and aminoplast crosslinking agent (Cymel®) were dissolved in one-third of the total solvent (PnP). The mixture was filtered through a membrane filter for ion removal. Then, the polydibutyltitanate and remaining two-thirds of the solvent were added. The final formulation was filtered through a particle filter.

TABLE 1

Protective Layer Formulation 1	
Polydibutyltitanate (obtained from DuPont)	24 g
Ethyl acetoacetate (obtained from Lonza)	31 g
Cyano acrylate (obtained from St.-Jean Photochemicals)	6.3 g
Cymel ® 303LF (obtained from Cytec Industries)	6.3 g
PnP (obtained from General Chemical Corp.)	332 g

[0043] 2. Preparation of Protective Layer Formulation 2

[0044] The ingredients used in this part are set forth in Table 2 below. The diketone ligand, chromophore, and aminoplast crosslinking agent were dissolved in one-third of the total solvent (PnP). The mixture was filtered through a membrane filter for ion removal. Then, the polydibutyltitanate, photo acid generator (TAZ-108™), and remaining two-thirds of the solvent were added. The final formulation was filtered through a particle filter.

TABLE 2

Protective Layer Formulation 2	
Polydibutyltitanate	24 g
Ethyl acetoacetate	31 g
Cyano acrylate	6.3 g
Cymel ® 303LF	6.3 g
TAZ-108 (obtained from Midori Kagaku Co.)	2.6 g
PnP	332 g

[0045] 3. Preparation of Protective Layer Formulation 3

[0046] The ingredients used in this part are set forth in Table 3 below. The polydibutyltitanate, ethyl acetoacetate, and 1,1,1-tris(hydroxymethyl)ethane in Table 3 were added to a glass reactor equipped with shaft-drive stirrer, water-cooled condenser, and nitrogen sweep. The reactor was heated to 100° C. with stirring for 20 hours, then cooled to 30° C. The solvent, PnP, was finally added and mixed at room temperature.

TABLE 3

Protective Layer Formulation 3	
Polydibutyltitanate	5.2 g
Ethyl acetoacetate	6.5 g
1,1,1-Tris(hydroxymethyl)ethane (obtained from Aldrich)	1.3 g
PnP	87 g

[0047] 4. Preparation of Protective Layer Formulation 4

[0048] The ingredients used in this part are set forth in Table 4 below. All the ingredients were mixed and dissolved in the solvent. The mixture was filtered through a particle filter.

TABLE 4

Protective Layer Formulation 4	
Polydibutyltitanate	37 g
Ethyl acetoacetate	17 g
1,1,1-Tris(hydroxymethyl)ethane	5.2 g
Irgacure ® 184 (obtained from Ciba Specialty Chemicals)	26 g
PGMEA (obtained from Harcros Chemicals)	722 g

Example 2

Protective Layer Process Conditions

[0049] The protective layer formulation prepared in Part 1 of Example 1 was applied to a silicon substrate and processed under the following conditions shown in Table 5.

TABLE 5

Process Conditions	
Spin speed	2000 rpm
Spin time	60 sec
Bake temperature	205° C.
Bake time	60 sec

[0050] A photoresist (a non-chemically amplified photoresist, sold under the name Ultra i-123 by Shipley) was diluted with ethyl lactate at a weight ratio of 1:6 to achieve a photoresist composition having a solids content of about 2.2% by weight. The photoresist was applied to the protective layer under the following process conditions: 2000 rpm spin coat; 90° C./60 sec soft bake; 115° C./90 sec post-exposure bake (PEB). FIG. 2 shows cross-sections of dense line patterns (1:1) obtained at 365 nm (exposure dose—110 mJ/cm²) on an i-line stepper (GCA Model 3300, NA 0.43) with the protective layer of this invention and the diluted photoresist thickness. The protective layer thickness was 76 nm. The photoresist and protective layer were developed with 0.26 N TMAH.

[0051] FIG. 3 shows cross-sections of line patterns (0.6 micron dense L/S (1:1)) obtained with a photoresist thickness of 24 run (using the thinned photoresist described at the beginning of this Example). The protective layer formulation of Part 1 Example 1 was used, and the protective layer thickness was 76 nm. The process conditions were the same as those shown in Table 5. The photoresist process conditions were: 5000 rpm/60 sec spin coat; 90° C./60 sec soft bake; 115° C./90 sec PEB. The remaining conditions were the same as those discussed in the preceding paragraph with respect to FIG. 2. Clear protective layer patterns were achieved.

[0052] FIG. 4 shows a cross-section of dense (1:1) line/space patterns obtained on a KrF stepper (Microscan III SVGL/ASML, NA=0.6, dose=47 mJ/cm²). To achieve these patterns, the protective layer formulation prepared in Part 4 of Example 1 was applied and processed under the conditions shown in Table 5. A commercially available chemically amplified KrF photoresist (sold under the name UV210 by Shipley) was diluted with ethyl lactate at a weight ratio of 35:65. The diluted photoresist was applied to the protective layer at 2000 rpm/60 sec and baked at 90° C./60 sec to yield a photoresist layer having a thickness of about 100 nm. The wafer was then exposed through a photomask at a wavelength of 248 nm and baked at 130° C./90 sec. The photoresist together with the protective layer was developed with 0.26 N TMAH.

Example 3

Pattern Transfer from Protective Layer to Substrate

[0053] The protective layer formulation prepared in Part 1 of Example 1 was applied to the surface of poly silicon. The protective layer was processed with the conditions in Table 5, and yielded a protective layer with a thickness of 75 nm. A photoresist layer was applied on top of the protective layer and was subsequently baked at 90° C./60 sec to yield a photoresist layer having a thickness of about 45 nm. The photoresist layer was then exposed through a photomask at a wavelength of 365 nm and baked again at 130° C./90 sec. The exposed areas of the protective layer and photoresist were removed by a 0.26 N TMAH solution. Patterns of the protective layer and thin photoresist, similar to the results of Example 2, were obtained. The wafer with line/space patterns of the protective layer on top of 320-nm poly silicon was subjected to reactive ion etch (RE) with following conditions: chlorine (the etchant) 80 sccm; pressure 25 mTorr; and RIE power 250 W. The line/space patterns of the 75-nm protective layer were successfully transferred to the poly silicon substrate. FIG. 5 shows the etch result.

Example 4

Protective Layer Ion Implantation Barrier

[0054] The protective layer formulation prepared in Part 1 of Example 1 was applied to a silicon substrate. The protective layer was processed with the conditions in Table 5. A photoresist was applied on top of the protective layer and subsequently baked at 90° C./60 sec to yield a photoresist having a thickness of about 45 nm. The photoresist layer was then exposed through a photomask at a wavelength of 365 nm and baked again at 130° C./90 sec. The exposed areas of the protective layer and photoresist were removed by a 0.26 N TMAH solution. The resulting patterns of the protective layer and thin photoresist were subjected to oxygen implantation at 10^{14} ions/cm^2 and 50 KeV. FIG. 6 shows the intact protective layer patterns after implantation.

Example 5

Etch Selectivities of Protective Layer Over Photoresist and Poly Silicon

[0055] The protective layer formulations prepared in Parts 1 and 3 of Example 1, together with a commercial photoresist and poly silicon substrate, were etched with oxygen and chlorine. Data in Table 6 show that the protective layers of this disclosure are truly etch barriers.

TABLE 6

Etch Rates and Parameters

	Oxygen (sccm)	Chlorine (sccm)	RIE Power (W)	Pressure (mTorr)	Etch Rate (nm/sec)
Formulation 1 of Example 1		80	250	25	0.035
Formulation 3 of Example 1	50		50	50	0.1
		80	250	25	0.029
UV ™ 210ª	50		50	50	4.9
Poly silicon		80	250	25	10

ªobtained from Shipley.

We claim:

1. A method of forming a precursor structure for use in microelectronic applications, said method comprising the steps of:

providing a substrate having a surface;

applying a protective layer to said substrate surface; and

applying a photoresist to said protective layer, said photoresist having a thickness of less than about 150 nm.

2. The method of claim 1, further comprising the step of applying an intermediate layer to said substrate surface prior to said protective layer applying step.

3. The method of claim 2, wherein said intermediate layer is a planarizing layer.

4. The method of claim 1, wherein said protective layer has an n value of at least about 1.2 and a k value of at least about 0.

5. The method of claim 1, wherein said protective layer is photo-sensitive.

6. The method of claim 1, further comprising the step of curing said protective layer.

7. The method of claim 1, further comprising the step of:

exposing at least a portion of said photoresist to activating radiation; and

developing said exposed photoresist.

8. The method of claim 7, wherein:

said protective layer has an initial solubility in a base developer;

said exposing step further comprises exposing at least a portion of said protective layer to activating radiation; and

said exposed protective layer portion has a final solubility in a base developer, said final solubility being greater than said initial solubility.

9. The method of claim 7, wherein said developing step comprises developing said exposed photoresist with an aqueous developer.

10. The method of claim 9, wherein said developing step results in the removal of said protective layer from areas adjacent said exposed portion of said photoresist.

11. The method of claim 9, wherein said aqueous developer is selected from the group consisting of tetramethyl ammonium hydroxide and KOH developers.

12. The method of claim 1, wherein said substrate has a hole formed therein, said hole being defined by a bottom wall and sidewalls, and said applying step comprises applying said protective layer to at least a portion of said bottom wall and sidewalls.

13. The method of claim 1, further including the step of baking said protective layer, after said protective layer applying step, at a temperature of from about 130-250° C.

14. The method of claim 13, wherein said protective layer has a thickness of from about 20-150 nm.

15. The method of claim 1, wherein said photoresist is formed from a composition comprising less than about 5% by weight solids, based upon the total weight of the composition taken as 100% by weight.

16. The method of claim 1, wherein said protective layer comprises:

a solvent system; and

a polymer dispersed or dissolved in said solvent system, said polymer including recurring units having the formula
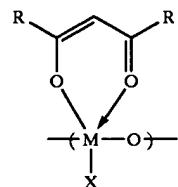
wherein X is selected from the group consisting of light-attenuating moieties and polyols, M is a metal, and each R is individually selected from the group consisting of hydrogen, alkyls, aryls, alkoxys, and phenoxys.

17. The method of claim 1, wherein said substrate is selected from the group consisting of silicon, polysilicon, silicon oxide, silicon nitride, silicon oxynitride, gallium

arsenide, aluminum, tungsten, titanium, titanium-tungsten, nickel, copper, and gold substrates.

18. The combination of:

a substrate having a surface;

a protective layer adjacent said surface; and

a photoresist adjacent said protective layer, said photoresist having a thickness of less than about 150 nm.

19. The combination of claim 18, further comprising an intermediate layer between said substrate surface and said protective layer.

20. The combination of claim 19, wherein said intermediate layer is a planarizing layer.

21. The combination of claim 18, wherein said protective layer has an n value of at least about 1.2 and a k value of at least about 0.

22. The combination of claim 18, wherein said protective layer is photo-sensitive.

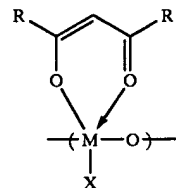**23.** The combination of claim 18, wherein said protective layer is cured.

24. The combination of claim 18, wherein said protective layer has a thickness of from about 20-150 nm.

25. The combination of claim 18, wherein said photoresist is formed from a composition comprising less than about 5% by weight solids, based upon the total weight of the composition taken as 100% by weight.

26. The combination of claim 18, wherein said protective layer is formed by curing a composition comprising:

a solvent system; and

a polymer dispersed or dissolved in said solvent system, said polymer including recurring units having the formula

wherein X is selected from the group consisting of light-attenuating moieties and polyols, M is a metal, and each R is individually selected from the group consisting of hydrogen, alkyls, aryls, alkoxys, and phenoxys.

27. The combination of claim 18, wherein said substrate is selected from the group consisting of silicon, polysilicon, silicon oxide, silicon nitride, silicon oxynitride, gallium arsenide, aluminum, tungsten, copper, titanium, titanium-tungsten, nickel, and gold substrates.

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